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## PROVISIONAL SPECIFICATION

Invention Title: "ALUMINOSILICATES OF ZEOLITE N  
STRUCTURE"

The invention is described in the following statement:

## ALUMINOSILICATES OF ZEOLITE N STRUCTURE

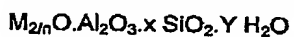
### FIELD OF THE INVENTION

This invention describes a process for the production of alkali metal aluminosilicates, in particular crystalline aluminosilicate zeolites, having the N structure. These materials have value when used as components of ion-exchange processes for example as in water and wastewater treatment, detergent formulation, heterogeneous catalysis preparation, controlled release fertilisers and for adsorption/absorption. These materials also have other properties that provide additional benefits when used for these purposes. These aluminosilicates will be referred to as zeolite N in this specification.

### BACKGROUND OF THE INVENTION

Zeolites are three-dimensional, microporous, crystalline solids with well-defined structures that contain aluminium, silicon, and oxygen in a regular framework; cations and water are located within the framework pores. Silicon and aluminium atoms are tetrahedrally coordinated with each other through shared oxygen atoms. Zeolites are natural minerals that are mined in many parts of the world. However, many commercially utilised zeolites are synthetic.

A representative formula for a zeolite is:



where M = the exchangeable cation, n represents the cation valence, x is equal to or greater than 2 and Y is the level of hydration. Zeolites are classified in terms of their framework structure and at present about 136 distinct zeolite forms are known. Of these forms, less than ten are currently used for commercial purposes.

An important property of zeolites is the silicon to aluminium ratio in the framework. The presence of aluminium in the structure results in a negative framework charge which is balanced by an external cation (positively charged) species. The majority of zeolites have an Si:Al ratio above 3. However, for commercial applications such as ion-exchange, gas adsorption/separation and catalysis an Si:Al ratio about, or near to, 1 is highly desirable (the theoretical limit in such structures is 1 due to Lowenstein's rule). Only a few zeolites with Si:Al ratio between 1.0 and 2.0 have been synthesized at industrially relevant scales. Such zeolites include Zeolite A, Zeolite P, Zeolite X and Zeolite F.

The synthetic zeolite K-F originally described by Barrer *et al.*, (1953) and Barrer and Baynham (1956) is structurally defined by Baerlocher and Barrer (1974) in the sodium exchanged form. Further work on potassium-derived zeolites by Barrer and Marcilly (1970) define salt-bearing forms of zeolite including zeolite N. These syntheses are

generally via hydrothermal crystallisation or re-crystallisation of minerals or gels at temperatures greater than 100°C in an autoclave.

The crystal structure of zeolite N has been determined by Christensen and Fjellvag (1997) using synchrotron X-ray powder diffraction. This work, and a subsequent study (Christensen and Fjellvag, 1999), used a hydrothermally treated mixture of zeolite 4A, sodium aluminosilicate gel and potassium chloride at 300°C for 7 days to produce high yields of well-crystallised zeolite N. These structural studies show that zeolite N is pseudo-tetragonal with an EDI-type structure and crystallographically distinct from zeolite F. The zeolite N structure is orthorhombic with space group I222. Cell dimensions based on this refinement of the zeolite N structure are  $a = 990.41(2)$ ,  $b = 988.60(2)$ ,  $c = 1309.00(2)$  with  $Z=1$  for the potassium form with composition  $K_{12}Al_{10}Si_{10}O_{40}Cl_2 \cdot 8H_2O$  (Christensen and Fjellvag, 1997).

Zeolite N and O species have been formed by the hydrothermal recrystallisation of analcite and leucite with excess KCl (species N) or KBr (species O) as described by Barrer and Marcilly (1970). However, the yield of zeolite N for this process is low (< 25%) and high temperatures (*i.e.* ~450°C) are required for a good yield. Because recrystallisation proved difficult, Barrer and Marcilly (1970) developed a synthesis procedure from gels using potassium halide salts at temperatures above 100°C. Poorly crystallised phases formed at 100°C while well-crystallised phases formed at  $T > 200^\circ\text{C}$ . For this zeolite type,  $SiO_2:Al_2O_3$  ratios between 2 and 3 are preferred for the starting gels. Barrer and Marcilly (1970) proposed that the well-crystallised zeolite K-F(Cl) form contained structural KCl and thus, by inference, is zeolite N as described by Christensen and Fjellvag (1997).

Barrer and Marcilly (1970) obtained good yields of zeolite K-F(Cl) by hydrothermal synthesis from crystalline Linde Na-X at temperatures between 200°C and 400°C. Higher yields were obtained at temperatures close to 400°C. Barrer and Marcilly (1970) found that this synthesis procedure using the clay mineral kaolinite yielded only kallophillite at  $T > 200^\circ\text{C}$  and did not produce zeolite N from a kaolinite parent even though the  $SiO_2:Al_2O_3$  ratio is commonly between 2 and 3 for this mineral.

The nomenclature for zeolites has evolved over a period of decades since the early discovery of hydrothermal synthesis routes by Barrer. The term "zeolite N" as disclosed in US 3,414,602 and US 3,306,922 was initially used to designate an ammonium or alkyl ammonium substituted cationic species. However, this nomenclature to describe alkyl ammonium or ammonium substituted species is no longer practised (Szostak, 1998). Sherman (1977) describes the confusion at the time with nomenclature for eleven zeolites synthesised in the  $K_2O-Al_2O_3-SiO_2-H_2O$  system and clarifies relationships for

Linde F and zeolite K-F. However, zeolite N is not described in this work by Sherman (1977). Using the structural classification for the zeolite class of minerals – both natural and synthetic – zeolite N is a sub-class of the EDI type zeolite framework based on the type mineral edingtonite (Christensen and Fjellvag, 1997).

A process for the production of X-ray amorphous aluminosilicate or kaolin derivatives obtained by the chemical modification of clay minerals and other aluminium-bearing minerals is described in US 6,218,329 B1, US 6,218,329 B2 and US 5,858,081. In these disclosures, the chemical modification of clay minerals to form aluminosilicate or kaolin derivatives involves the mixing of a caustic reactant in the form of an alkali halide, alkali metal halide, alkali hydroxide or alkali metal hydroxide, or combinations of these reactants, with a clay such as kaolin in the presence of water at temperatures less than 200°C and preferably less than 100°C.

As disclosed in US 6,218,329 B1; US 6,218,329 B2 and US 5,858,081, for certain potassium-dominant reactions, minor amounts of zeolite and other crystalline aluminosilicates such as kalisite and kaliophilite are formed. However, the predominant phase is an amorphous (*i.e.* non-crystalline) aluminosilicate.

The potential for application of zeolites or related aluminosilicate materials as adsorbents of ammonium ions in wastewater streams is well known (US 4,695,387; US 6,080,314). Due primarily to cost and availability considerations, the natural zeolite, clinoptilolite, has received the majority of attention with respect to ion-exchange removal of ammonium ions from wastewater (Cooney *et al.*, Separation Science and Technology, **34**, 2741-2760, 1999). Unfortunately, clinoptilolite is characterized by a low exchange capacity for ammonium ions (typically < 150 mmol  $\text{NH}_4^+$ /100g of material) and is not selective towards ammonium adsorption in the presence of competing cations such as alkali and alkaline earth ions.

Efforts have been made to improve the ammonium selectivity, for example Carnahan and Knotts (WO 9104948) disclosed that heating the clinoptilolite to a temperature of 600 °C to 800°C for at least one hour could result in an increase in ammonium ion selectivity while Booker *et al.* (Water Sci. Tech., **34**, 17-24, 1996) showed that the Na-exchanged form provided highest adsorption capacity for ammonia compared with a Ca- or Mg-exchanged form. The work by Komarowski and Yu (Environmental Tech., **18**, 1085-1097, 1997) showed that Na-exchanged clinoptilolite has a maximum uptake of 3.2 to 3.7  $\text{mgNH}_4^+$ /g zeolite at pH 5.5 for a  $\text{NH}_4\text{Cl}$  solution. The uptake value for clinoptilolite decreased to  $\leq 2.0$   $\text{mgNH}_4^+$ /g zeolite at pH ~ 7.0. Actual wastewaters commonly contain competing ions such as  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$  in a carbonate or sulphate rich solution at pH between 6.0 and 7.5. The low uptake values and decreased performance of clinoptilolite

at higher pH provides the key to why it has not been widely used in commercial applications.

Alternatively, Breck (US Patent 3,723,308) discovered that zeolite F was characterized by not only a high cation exchange capacity for ammonium ions but also exhibited selectivity for ammonium ions in the presence of competing cations such as calcium, magnesium, sodium and potassium; and phosphate and sulphate anions. Indeed, zeolite F could adsorb in excess of 4 times the quantity of ammonium ions adsorbed by clinoptilolite. Moreover, the separation factor for ammonium ions was 3.6 for zeolite F compared to 1.7 for the natural zeolite, thus confirming the improved ammonium ion selectivity for zeolite F. Similarly, Hueller and Hantschel (DE 3924565) demonstrated that zeolite F synthesized using glassy waste materials from power plants showed reasonable adsorption capacity for ammonium ions in wastewater in the presence of calcium and magnesium ions. A comparative study on ammonium ion exchange in the presence of alkali metal ions such as calcium and magnesium by Sherman and Ross (US 4,344,851) demonstrated that phillipsite-type zeolites (e.g. Linde Type W zeolite) possess an unusual capacity and selectivity for ammonium ion.

In column experiments, Sherman and Ross demonstrate that zeolite F, whilst initially showing a high capacity for ammonium, rapidly loses this capacity (to less than 50% the initial values) on subsequent sodic regenerations using standard methods. However, zeolite W, whilst not showing a high capacity, increased its capacity by up to 40% of the initial values with further regeneration cycles. The loss of ammonium adsorption capacity by zeolite F after regeneration is a significant hindrance to full-scale commercial utilisation in typical wastewaters.

Araya and Osinga (WO 97/17300) discovered that zeolite P characterized by a  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio  $\sim 2$  had a cation exchange capacity (CEC) for ammonium ions of 500mmol  $\text{NH}_4^+$ /100g of material, compared to a CEC value of 150mmol  $\text{NH}_4^+$ /100g material for clinoptilolite. When sodium ions are present in the ammonium solution, zeolite P adsorbed up to 330mmol  $\text{NH}_4^+$ /100g whereas clinoptilolite adsorbed 60mmol  $\text{NH}_4^+$ /100g of material.

Nevertheless, it can be calculated that the theoretical CEC value for a zeolite of  $\text{SiO}_2/\text{Al}_2\text{O}_3 \sim 2$  and exchanged with sodium cations, on a dry basis is approximately 700mmol  $\text{NH}_4^+$ /100g of material. Therefore, it can be seen that zeolite P does not achieve maximum loading of ammonium ions. Furthermore, Araya and Osinga (WO 97/17300) did not demonstrate that zeolite P is selective for ammonium ions in the presence of calcium and magnesium ions which are typically present in wastewater

streams. As zeolite P has a well-known high capacity for calcium ions (US 5,560,829) the use of this material for removal of ammonium ions is not commercially attractive.

The prior art by Breck (US 3,723,308), Sherman and Ross (US 4,344,851) and others, assess the performance of zeolites for ammonium ion concentrations less than 50mg/L which, as described, is typical of inlet wastewater streams at sewage treatment plants or, at lower levels (e.g. less than 10mg/L), typical of the outlet streams from sewage plants with primary and secondary treatment processes. Other wastewater streams at sewage treatment plants, as well as at industrial/chemical plants, contain ammonium ion at concentrations greater than 100mg/L up to 1,500mg/L or more. For example, waste streams from anaerobic digestion processes (within a sewage treatment plant or from a landfill) typically contain high levels of ammonium ion (between 100mg/L and 2,000mg/L) due to the actions of bacteria in these processes. It is therefore evident that to date there has been no demonstration of the successful performance of zeolite materials under these high levels of ammonium ion with or without competing ions such as calcium and magnesium.

Contamination of water by heavy metals such as lead, cobalt, nickel, zinc, chromium and copper represents a serious environmental issue and, as a consequence, environmental protection authorities have imposed limits relating to metal ions in solutions discharged to the environment. There exist several methods such as precipitation, adsorption and ion-exchange to treat for metal ion contamination in water. Ion-exchange of metal ions is particularly attractive in that engineering design and practice are scaleable and cost effective.

Aluminosilicate materials such as clays and selected zeolites have been studied for their ability to remove metal ions from solution. Yavuz *et al.* (O. Yavuz, Y. Altunkayanak and F. Guzel, Water Research, 37 (2003) 948-952) reported the removal of metal ions such as copper, nickel, cobalt and manganese from aqueous solution by kaolin clay material. However, the metal loading capacity for kaolin is unacceptably low (ca. 0.4 to 10.8 g/kg) for commercial application. Suraj *et al.* (G. Suraj, C.S.P. Iyer and M. Lalithambika, Appl. Clay Sci., 13 (1998) 293-306) attempted to improve the properties of kaolin clay by thermal activation followed by acid treatment. Despite these modifications to the clay material, metal ion loadings are still low (ca. 1.1 to 1.5 g/kg).

Zeolites have received attention due to their theoretically higher cation exchange capacity for metal ions. Mondale *et al.* (K.D. Mondale, R.M. Carland and F.F. Aplan, Minerals Engineering, 8, 535-548, 1995) compared the metal ion exchange capacities of various natural and synthetic zeolites such as Clinoptilolite, Mordenite, Zeolite 3A, Zeolite

4A, Zeolite 5A, Chabazite, 13X and Erionite. A large variation in the cation exchange capacity of these zeolites was demonstrated.

In practical situations, calcium ions are almost always present in significant concentrations in the wastewater or water sample to be treated. Calcium ions can be present due to either natural causes (lake or river water, rain water, bore water *etc* are commonly "hardened" by the presence of calcium ions) or introduced as a consequence of precipitation methods involving the use of lime (a common treatment method used to remove some metal ions in solution such as iron). Therefore, it is commercially important to demonstrate selectivity of the zeolite material for the metal ion of concern in the presence of calcium ions.

Moreno *et al.* (N. Moreno, X. Querol, C. Ayora, C.F. Pereira and M. Janssen-Jurkovicova, *Environ. Sci. Technol.*, 35, 3526-3534, 2001) studied the behaviour of zeolites A and P for removal of a wide range of metal ions in mine water, in the presence of excess concentrations of calcium and magnesium ions. Notably, these zeolites are shown to be efficient at the removal of calcium and magnesium ions and thus, not selective towards the contaminant metal ions of interest. As a result, it was found by these authors that the amount of zeolite solid required for metal ion removal was unacceptably large for commercial application. Ouki and Kavannagh (S.K. Ouki and M. Kavannagh, *Waste Management & Research*, 15, 383-394, 1997) reported that the natural zeolites clinoptilolite and chabazite are also not selective in the presence of calcium ions albeit to a seemingly lesser extent than synthetic zeolites. Nevertheless, these natural zeolites do not display high cation exchange capacities and thus are not commercially attractive.

Ruminant animals (e.g. cattle, sheep and goats) can manufacture protein amino acids from non-protein nitrogen compounds such as urea. Compounds like urea for example, are significantly cheaper than conventional high protein feed. Therefore, there is an economic incentive to replace vegetable protein feed with non-protein nitrogen substances. However, the quantity of non-protein nitrogen is restricted as a consequence of the fact that ammonia (or ammonium ions) is produced by digestion processes.

Ammonia is regarded as a cell toxicant and thus, is detrimental to the health of the animal. The use of zeolites to moderate the concentration of ammonia in the rumen when an animal is fed non-protein nitrogen is known (US 4,393,082). The important issue for commercial application is that the zeolite material must be selective to ammonium ions in the presence of competing cations such as calcium, sodium and potassium which are present in both the animal saliva and animal ruminal fluid.



Breck (US 3,723,308) investigated a range of zeolitic materials including Zeolite A, Zeolite X, Zeolite Y, Zeolite F, Chabazite and Clinoptilolite for ammonium selectivity from an artificial ruminal fluid composition. Zeolite F was shown to be the most selective zeolite from this latter group and a similar conclusion was reported in US 4,393,082. In this prior art, zeolite F was discovered to be the most selective zeolite for ammonium ions under these conditions. Unfortunately, no absolute data are presented to show the precise amounts of calcium, potassium and sodium exchanged by these zeolites.

Many odour problems such as those associated with intensive farming of pigs, poultry and the like involve the release of ammonia. Therefore, it is desirable to find means by which to regulate these offensive emissions of ammonia. The use of zeolites has been mentioned due to their potential to adsorb ammonia at acid sites on their framework. Clinoptilolite has received most attention albeit results appear to be somewhat inconclusive and unsatisfactory.

The fertilizer industry faces a permanent challenge to improve the efficiency of its products. This is done either through improvement of fertilizers already in use or through development of new specific fertilizer types. An ideal fertilizer should have at least the following three characteristics:

- Requires a single application throughout an entire growing season to supply the necessary amount of nutrients for optimum plant growth,
- Has a high maximum percentage recovery in order to achieve a higher return to the production input
- Has minimum detrimental effects on soil, water and atmospheric environments and preferably, has beneficial effects on soil properties (such as pH, salinity *etc.*).

Slow, and in particular, controlled release fertilizers may meet these requirements. Slow and controlled release fertilizers usually contain a plant nutrient in a form which either (1) delays availability for plant uptake and use after application, or (2) is available to the plant significantly longer than a reference "rapidly available nutrient fertilizer" such as ammonium nitrate or urea.

The natural zeolite, clinoptilolite, has been studied as a controlled release fertiliser due to its apparent ability to exchange ammonium, potassium and trace metal cations which are essential for plant growth. However, due to its low cation exchange capacity, it is not an ideal commercial material.

#### PREFERRED OBJECTS OF THE INVENTION

Preferred objects of this invention are:

1. To discover a material that can not only efficiently adsorb ammonium and certain metal ions in a number of environments (including wastewater and soils), but is selective towards ammonium and certain metal ions present in a range of concentrations in the presence of common alkaline earth and alkali metal ions such as calcium, magnesium, sodium and potassium;
2. To discover materials with improved ion exchange capacity and the ability to release required ions under appropriate controlled conditions for use or for recovery for applications such as nutrient release to plants and the production of concentrated forms of ammonium such as ammonium sulphate;
3. To discover materials with improved ammonia absorption characteristics for use in odour control applications and the uptake of ammonia gas under a range of conditions;
4. Contrary to the teaching of prior art in zeolite synthesis as described above and to the disclosed outcomes for production of aluminosilicate derivatives in US 6,218,329 B1; US 6,218,329 B2 and US 5,858,081 as described above, to produce high yields of high quality zeolite N by the chemical reaction of potassic caustics with kaolin or suitable aluminosilicate in the presence of chloride ions at temperatures  $< 100^{\circ}\text{C}$ ;
5. It is another object of the invention to produce the potassic form of zeolite N as well as the sodium and ammonium forms by ion exchange.
6. It is an object of the invention to produce a commercially effective process to manufacture the materials as described above for use in the market place. This object may be achieved by judicious choice of starting materials and reaction conditions and by the re-use of reaction liquor and of washing liquors in the manufacturing process;
7. It is thus a further object of this invention to provide a process for the effective commercial manufacture of zeolite N in potassic, sodic or other ionic form such as ammonium-exchanged zeolite N and mixtures of ions such as potassium and sodium forms;
8. It is a further object of this invention to show the use and application of zeolite N in the generic applications of ion exchange and absorption and the preparation of metal exchanged forms for use in heterogeneous catalysis.

#### SUMMARY OF THE INVENTION

The process to form zeolite N, disclosed in this invention, involves

- a. a potassium-rich or a potassium-rich and chloride-rich caustic solution with a pH greater than 10, more preferably a pH greater than 13 having a ratio of  $H_2O/Al_2O_3$  between 30 and 150 and preferably between 45-55,
- b. heating of the caustic solution to a temperature between 55°C and 120°C, preferably between 80°C and 95°C,
- c. addition of an aluminosilicate solid, preferably kaolin or a material with Al:Si ratio between 1.0 and 3.0, preferably 1.0 and 1.5, but other ratios may be possible, to the caustic solution
- d. reacting the resultant mixture at the described temperature for a time between 1 minute and 100 hours, preferably between two hours and eight hours, until the formation of a product corresponding to zeolite N as determined by X-ray diffraction or other suitable characteristic is achieved and
- e. separation of the solid zeolite N from the caustic liquor.

Once the product is formed, additional procedures for commercial manufacture may comprise

- f. washing of the zeolite N product to remove excess salts followed by subsequent drying of the solid product
- g. re-use of the caustic liquor as part of a caustic solution for subsequent production of additional zeolite N by the same process and
- h. re-use of the washing solution for subsequent production of zeolite N by the same process.

The reaction conditions for production of zeolite N as disclosed in this invention are surprisingly and significantly different from prior art and are not taught by conventional practice (Szostak, 1998). The compositions and procedures for this process are unlike those described by prior art. Highly preferred and specific starting compositions and reaction conditions to produce zeolite N in accordance with the invention are given in Table 1. Table 2 refers to a comparison of reaction conditions for selected zeolites produced by prior art.

Other preferred ratios of reagents used in the solution of step (a) above may comprise

- i.  $K/(K+Na)$  between 0.2 and 1.0, preferably between 0.6 and 1.0 and
- ii.  $Cl/SiO_2$  between 0.0 and 7.0, preferably between 0.8 and 2.0 and
- iii.  $(K+Na-Al)/Si$  between 2.66 and 20.00, preferably between 3.0 and 5.0,

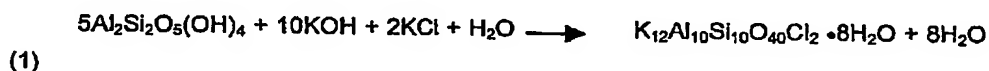
In Table 1, specific examples of the present invention (Examples 1,4,5,6 and 8) are compared with the only other prior art for production of high quality zeolite N (Christensen and Fjelvag, 1997). In this comparison, the present invention produces zeolite N at lower temperature (95°C compared to 300°C), lower water content ( $H_2O/Al_2O_3 < 55$  compared

with  $\text{H}_2\text{O}/\text{Al}_2\text{O}_3 > 200$ ), for a shorter reaction time (6 hours compared to 7 days) and with less alkaline earth salt ( $\text{KCl}/\text{Al}_2\text{O}_3$  or  $\text{NaCl}/\text{Al}_2\text{O}_3 < 3.5$  compared with  $\text{KCl}/\text{Al}_2\text{O}_3 > 12$ ).

Table 1 shows that alternative reaction parameters by which this synthesis procedure may be described such as  $\text{Cl}/\text{SiO}_2$  and  $\text{K}/(\text{K}+\text{Na})$  and  $(\text{K}+\text{Na}-\text{Al})/\text{Si}$  (*i.e.* in their totality), are markedly different from prior art. These alternative reaction parameters are derived from, and dependent upon, the molar values for the respective oxides or halides used in the batch composition.

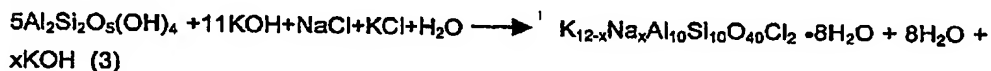
Table 2 shows that Barrer *et al.* (1953) did not produce high yields of zeolite N, but rather, produced mixtures of kalsilite and zeolite N or leucite and zeolite N. In their work, Barrer *et al.* (1953) used higher temperatures ( $450^\circ\text{C}$ ), longer times (1 – 2 days) and higher quantities of water and potassium salt than used in the current invention. Barrer and Marcilly (1970) used a stoichiometric amount of KOH and a high excess of KCl but, contrary to the present invention, did not produce zeolite N from a kaolin starting material which is a preferred starting material in the present invention. In the case of Barrer and Marcilly (1970) and Christensen and Fjervag (1997), the amount of KCl is in excess by more than twenty-five times but KOH is either present in stoichiometric quantities or not present in the reaction mix.

Contrary to the work of Barrer and Marcilly (1970) and Christensen and Fjervag (1997), the process of the present invention involves an excess of both KOH and KCl or an excess of potassium at high  $\text{OH}^-$  concentration. The percentage excess of each of these reagents can be determined by reference to the stoichiometric reaction to produce zeolite N:



Accordingly, with an excess of KOH in the reaction mix, the quantity of KCl required for production of zeolite N in high yield by this method is reduced.

Examples of stoichiometric reactions to form zeolite N include but are not limited to:



Reactions (1), (2) and (3) are described as Examples 1, 3 and 4 below. Reactions (2) and (3) imply that substitution of Na for K ion can occur in the zeolite N structure as demonstrated by the data in Table 5.

The reaction mix may be viscous with values ranging between 2,000 centipoise and 150 centipoise at 45°C over the range of spindle rotations from 5rpm to 100rpm at atmospheric pressure using a Brookfield viscometer. This viscosity may occur through use of a low proportion of solution (for example, water) in the reaction mixture and a high proportion of solids.

The disclosed process results in an aluminosilicate of zeolite N structure as shown in Table 4 possessing the following properties:

- (a) cation exchange capacity ranging from 100meq/100g to 600meq/100g, preferably greater than 300meq/100g, for ammonium ions over concentrations ranging from 5mg/L to 10,000mg/L,
- (b) selectivity for exchange of ammonium ions in the presence of alkaline earth ions in aqueous solutions ranging from 75% to 100%
- (c) capacity to re-exchange alkaline earth metal ions from solutions ranging in concentration from 0.1M to 2.0M, preferably between 0.4M and 1.5M when in an ammonium-exchanged form
- (d) removal rate of ammonium ranging between 75% and 100%, preferably between 90% and 100%, from ammonium-loaded zeolite N using a caustic regenerant solution
- (e) selectivity for exchange of metal ions such as copper, cadmium, zinc, nickel and cobalt in the presence of alkaline earth ions in aqueous solutions ranging from 50% to 100%
- (f) capacity to absorb ammonium gas between 25°C and 100°C
- (g) absorption capacity for oil ranging from 50g/100g to 150g/100g, preferably between 80g/100g and 140g/100g and
- (h) BET surface area values greater than 5m<sup>2</sup>/g.

A specific feature of zeolite N produced by the methods disclosed in this invention is the higher surface area value for powders compared with zeolites of comparable Si:Al ratio. In addition, the surface area consists predominantly of external surfaces. The surface area – as measured by conventional BET adsorption/desorption isotherms – for zeolite N is higher than that for zeolite 4A (see Table 7) and suggests that the primary particle sizes for zeolite N made by the methods described in this invention are smaller than for particles produced by conventional hydrothermal crystallisation methods. The invention may include within its scope zeolite N when produced by the process of the invention as well as Zeolite N having properties not described in the prior art.

#### ADVANTAGES OF THE INVENTION

The zeolite structure determines many useful properties for commercial application due to the variation of micropores (*i.e.* pores < 2.0nm size) within crystals and the existence of mesopores (*i.e.* 2.0nm < pores < 100nm) due to the aggregation of crystals. These pores in zeolites are directly related to composition and crystal structure. Compositions and crystal structure parameters for selected zeolites are listed in Table 3.

The present invention relating to the process to make zeolite N offers the following advantages:

1. high yields of zeolite N (achieve >90%) in large volume production
2. temperature of reaction is low (*i.e.* < 100°C) and reaction times are short (generally less than 1 day)
3. volumes of solution required are low (a factor of at least seven times less than other low temperature processes and four times less than known processes to make zeolite N before recycling of liquors)
4. feed liquor can be supplemented by recycled liquor from a previous batch of zeolite N production and
5. feed liquor can be supplemented by recycled wash water from a previous batch of zeolite N production.

For the present invention, recycled caustic reagent may be repeatedly used to produce high yield of zeolite N. The quantity of caustic liquor available for recycling after the initial reaction is dependant on the efficiency of solid-liquid separation technique used. The efficiency of filter pressing, centrifugation or other such separation techniques will be appreciated by those skilled in the art. The amount of make-up material required to add to the reaction mixture to produce the required aluminosilicate derivative is determined by analysis of the bulk composition of the liquor after separation from the solids and the volume of liquor available for recycling. The precise calculation of make-up material required for a recycling step can be determined by conventional analytical and chemical means readily envisaged by those skilled in the art.

Comparison of the caustic usage for the production of an equivalent mass of zeolite N as a result of (a) no recycle of caustic and (b) caustic recycle is summarised in Table 6. For Example 1 and the use of caustic recycle shown in Example 2, the quantity of caustic used with recycled liquor to produce 783 kg of zeolite N is reduced to 61% of the quantity used in reactions without recycle. The caustic to product ratio is reduced to the values shown in Table 6 when recycle of the liquor is included in the manufacturing process. The actual values of caustic make-up and recycled liquor for eight recycles of caustic as described in Example 2 are given in Table 7.

The procedure(s) in the examples below show recycling of caustic liquor up to eight times. It will be appreciated by those skilled in the art that a greater or lesser number of recycling steps can be implemented with similar outcome(s) to that provided in the examples below.

The examples in the present invention describe manufacture of aluminosilicate derivatives using potassium- and sodium-based caustics and salts such as potassium hydroxide, potassium chloride, sodium chloride, sodium hydroxide and mixtures thereof. Re-use of the separated caustic liquor after reaction to form aluminosilicate derivative is not limited to potassic forms of caustic reagents or their mixtures inasmuch as sodic or other suitable forms of caustic reagent, their mixtures (for example, sodium hydroxide and sodium chloride) and mixtures with potassic forms are suitable candidates.

Compared with conventional synthesis methods for potassic zeolites of the EDI topology, the ratios of caustic, water and anions required in comparison to the Al and Si source material, the time of reaction and the temperatures of formation are significantly reduced when using the process of the instant invention for high yields of zeolite N. It will be appreciated by those skilled in the art that alternative reaction mixes within the broad scope of the conditions established in this invention (for example, use of gels or liquid caustics of the appropriate composition) will result in similar advantages for zeolite N synthesis.

The present invention relating to the uses of zeolite N provide the following advantages:

1. a hydrophilic material with exceptional capacity to exchange ammonium ions from solutions compared with other existing aluminosilicates
2. a hydrophilic material with excellent selectivity for ammonium ion exchange in the presence of alkali metal ions including calcium and magnesium compared with existing aluminosilicates
3. capacity to be formed into granules suited to fixed bed exchange columns for ion exchange of alkali metal, ammonium, transition metal, rare earth and actinide metal ions
4. capacity for continuous re-use through cyclic regeneration of the material (as granules and as powders) using a caustic solution
5. improved capacity to remove ammonium ion from solutions and to absorb oil compared with existing aluminosilicates such as zeolites 4A, P, bentonite and kaolinite.

The uses of zeolite N, disclosed in this invention, include:

- a. the removal of ammonium ion from solution *via* ion exchange with the potassic, sodic or mixed cation form of zeolite N;

- b. the selective removal of ammonium ion from solution *via* ion exchange with the potassic, sodic or mixed cation form of zeolite N in the presence of competing solution ions such as calcium, magnesium, sodium, potassium, carbonate, chloride and sulphate;
- c. a capacity for regeneration of zeolite N (in either potassic, sodic or mixed form) such that the removal and selective removal of ammonium ion from solutions in "a" and "b" are maintained for more than four cycles
- d. improved removal of ammonium ion from solution (as defined in "a" and "b") compared to natural zeolites and synthetic zeolite A and other zeolites,
- e. higher absorption of oils and greases compared with natural zeolites, synthetic zeolites A, X, and P, the natural minerals bentonite and attapulgite (palygorskite) and amorphous silica and
- f. selective ion exchange of transition, rare earth and actinide metals in the presence of divalent calcium and magnesium ions.

Other uses of zeolite N, in its various ion-exchanged forms, include but are not limited to

- a. selective adsorption of gases such as hydrogen, helium or ammonia due to the specific size and shape of micropores in the framework structure;
- b. selective adsorption of ammonium in the intestines of ruminants and other foodstock animals (pigs, poultry) to enhance the digestive process;
- c. provision of large molecule compounds (such as proteins, amino acids, hydrocarbons) to specific environments (e.g. human or animal intestines; soils) *via* external mesopores whilst removing specific ions (such as ammonium);
- d. reduction of odours in animal feedlots, in animal housing and similar types of enclosed spaces;
- e. reduction of ammonium ion in saline and brackish environments such as mariculture and silviculture ponds;
- f. formation of active sites for catalytic reactions using solids with either Lewis acid or Bronsted acid (or both) sites such as may be used in heterogenous catalysis;
- g. formation of metal-exchanged aluminosilicate substrates for heterogenous catalysis reactions and
- h. removal of metallic poisons from active participation in specific catalytic processes such as hydrocarbon refining.

While the invention has been described in connection with a preferred embodiment, it is not intended to limit the scope of the invention to the particular form set forth, but on the contrary, it is intended to cover such alternatives, modifications, and equivalents as may



be included within the spirit and scope of the invention as defined by the appended claims.

## EXPERIMENTAL

Parameters critical to the successful synthesis of zeolites are (a) compositions and form of the reactants, (b) the temperature and time of reaction, (c) the effect of pH and anions other than  $\text{OH}^-$  and (d) processing conditions such as presence of "seed" materials, aging and stirring of the reaction mix and the order of mixing. These parameters and conventions for reporting synthesis conditions are described by Szostak (1998) and apply generally to hydrothermal crystallisation processes. However, as shown in the examples below, the production of zeolite N by this disclosure may not involve hydrothermal crystallisation processes.

For convenience and to define a phase stability region, reactions described herein have been performed at the same temperature ( $95^\circ\text{C}$ ) and similar water content ( $45 < \text{H}_2\text{O}/\text{Al}_2\text{O}_3 < 55$ ). However, having defined the general location of the phase field for zeolite N at these conditions, it will be appreciated by those skilled in the art that zeolite N may be produced under other experimental conditions of temperature, water content, reaction time and reaction mixture as demonstrated in Example 8.

Systematic evaluation of reaction variables for the preferred temperature ( $95^\circ\text{C}$ ) and water content ( $45 < \text{H}_2\text{O}/\text{Al}_2\text{O}_3 < 55$ ) in the presence of chloride ion and characterisation of the product(s) shows that the formation of zeolite N may be described by the ratios of reagents in the mixture. Examples of this are provided in Figures 1a-1c.

Figures 1a, 1b and 1c provide the phase field(s) for zeolite N production defined by the processes described in the examples below compared with that used by Christensen and Fjelvag (1997). The data in Figure 1, except for points designated with an open symbol (which includes the method described by Christensen and Fjelvag, 1997), are for a reaction temperature of  $95^\circ\text{C}$  for 6 hours.

Figure 1a shows the location of the zeolite N stability field in terms of cation ratio ( $f=\text{K}/(\text{K}+\text{Na})$ ; Bieniok *et al.*, 1996) plotted against excess alkalinity for examples in this disclosure compared with the synthesis by Christensen and Fjelvag (1997). The region described by Christensen and Fjelvag (1997) is significantly different from the regions for zeolite N described in this patent (Examples, 1, 3, 4, 5, 6 and 8) notwithstanding the factor of four difference in water content and the differences in temperature and type of reaction.

Figure 1b shows the phase field for excess alkalinity (defined by Bieniok *et al.*, 1996 as  $m=(K+Na-Al)/Si$ ) and chloride ion concentration. As with Figure 1a, the region described by Christensen and Fjelvag (1997) is significantly displaced from the regions for zeolite N described in this patent (Examples, 1, 3, 4, 5, 6 and 8). Figure 1c shows the excess alkalinity against water content for the reaction mix (*i.e.*  $H_2O/Al_2O_3$ ) and highlights the wide difference in water content between conventional hydrothermal synthesis and the method described in this disclosure.

In all cases, the production of zeolite N by the examples in this disclosure are significantly and surprisingly different to that described by Christensen and Fjelvag (1997).

#### Standard Procedures

For zeolite N reactions at bench and pilot plant scale, stainless steel reactors equipped with (i) a mixing blade, (ii) an external heating coil with thermocouple and (iii) a loose-fitting cover have been employed. For many reactions at scales >600g, samples of the mix are extracted during the reaction in order to measure standard parameters. Measurements of pH for these reaction mixtures were obtained from samples held between 60°C and 65°C.

Methods for characterisation of solid products include X-ray powder diffraction, surface area analysis, particle size, bulk elemental analysis and cation exchange capacity for ammonium ion. X-ray data were collected on a Bruker automated powder diffractometer using  $CuK\alpha$  radiation ( $\lambda=1.5406$ ) between  $5^\circ$  and  $70^\circ 2\theta$  at a scan speed of  $1^\circ 2\theta$  per minute using quartz as a calibration standard. JCPDS data were used to identify major phases in all samples. Cell dimensions for zeolite N samples were obtained by least-squares refinement from X-ray powder diffraction profiles. The number of peaks indexed and used for these refinements ranged between 28 and 43 per sample.

Surface area measurements were obtained on a Tristar 3000 instrument using the BET algorithm for data reduction and standard procedures for adsorption and desorption of nitrogen. Particle size is obtained on ultrasonically dispersed samples using conventional laser scattering techniques with a Malvern Mastersizer 2000 instrument. Bulk elemental analyses for major elements were obtained by inductively coupled plasma spectroscopy (ICP) using standard peak resolution methods.

Cation exchange capacities are determined experimentally for equilibrium exchange of ammonium ion in a 1M  $NH_4Cl$  solution. The procedure for determination of experimental CEC values described in this work is as follows:

1  
:  
1

0.5g of the material (zeolite N) is dispersed into 25ml of RO water and centrifuged at 3,000rpm for 10 minutes. Decant the supernatant for measurement of potassium ions.

Add 30ml of 1M  $\text{NH}_4\text{Cl}$  solution to the samples, shake to disperse particles and allow to agitate overnight for a period of 16 hours.

Centrifuge the equilibrated solution at 3,000rpm for 10 minutes, discard supernatant solution, add 30ml of 1M  $\text{NH}_4\text{Cl}$  solution, disperse solids by shaking and allow to agitate for two hours. Repeat this process for ammonium exchange a further time.

On the third centrifuge and discard of supernatant, add 30ml of absolute ethanol, shake to mix and then centrifuge for 10 minutes. Repeat ethanol wash process using an additional 30ml of absolute ethanol a further two times.

Add 30ml of 1M KCl solution to the samples, shake to disperse particles and allow to agitate overnight for a period of 16 hours.

Place samples in centrifuge for 10 minutes and decant supernatant into a clean 100mL volumetric flask. Add 30ml of 1M KCl solution, shake to mix and agitate for two hours. Repeat centrifuge, decant into clean 100mL flasks, add KCl and agitate for a further two times.

Make up each of the volumetric flasks with decanted supernatant to 100ml with 1M KCl solution.

Analyse all samples for ammonium ion concentration using the method by Kjeldahl (steam distillation). The cation exchange capacity for each sample is then calculated from these data.

This method for CEC determination when used on a well-known clay material (Cheto montmorillonite, AZ, Clay Minerals Society Source Clays SAz-1; van Olphen and Fripiat, 1979) as an internal calibration standard gives a CEC value of  $98.1 \pm 2.5$  meq/100g (54 analyses over a period of eighteen months). This value is consistent with the value for potassium exchange on SAz-1 of  $100 \pm 2$  meq/100g determined by Jaynes and Bingham (1986). All CEC values determined for the material(s) exemplified in this work are on a "wet weight" basis (*i.e.* no correction for dry weight of the material).

The method for determination of oil absorption is described in Example 19 and follows standardised procedures for detergent applications.

#### Examples and illustrative embodiment

Example 1: *Production of commercial quantities of zeolite N with excess KOH and KCl.*

75kg of 98% solid potassium hydroxide (Redox Chemicals, caustic potash Capota45, QLD Australia), 75kg of 98% solid potassium chloride (Redox Chemicals, POCHLO16, QLD Australia) and 250 litres of water supplied by a conventional domestic reticulated system are placed in a 500L stainless steel reactor tank. This caustic solution is stirred and heated to 95°C. While the solution is at this temperature, 75kg of kaolin (Kingwhite 65, supplied by Unimin Pty Ltd, Kingaroy, QLD Australia) is added to the reaction mix while stirring the solution. The reaction mix experiences a slight drop in temperature (to ~90°C) during the loading of kaolin. Depending on the quality of heating process employed, the reaction mixture may show temperature fluctuations of up to 5°C without significant loss of product quality. Small quantities of solid materials (approximately 50g) from the reaction mix are sampled at half-hourly intervals during this reaction and are characterised by conventional methods.

The reaction tank is partially covered with a stainless steel lid to aid with retention of heat and vapour(s). The reaction tank is maintained at ambient pressure during the production process. The pH of this reaction mix is generally greater than 14.0 and during the course of the reaction reduces to approximately 13.5. During the reaction process – approximately 1.5 hours to 3.5 hours after the kaolin has been added to the reactor – the viscosity of the mixture increases. Addition of small amounts of water at this time to aid mixing of the slurry may be undertaken though it is not necessary to achieve production of zeolite N.

After 5.5 to 6.5 hours of reactant mixing at temperatures  $95^{\circ}\text{C} \pm 5^{\circ}\text{C}$ , the reaction is stopped by reduction of the temperature to less than  $50^{\circ}\text{C}$  via cooling coils, addition of water or both methods and the resulting slurry is separated using a filter press into solid and liquid components. The solid aluminosilicate – zeolite N – is washed with water and then dried using conventional drying methods (such as a spray dryer) to form the final product with properties listed in Tables 4 and 5. The weight of zeolite N from this reaction was 98.3kg which represents a volume yield of greater than 90% for the stoichiometric reaction (1).

Characterisation of the material using standard methods such as X-ray diffraction, bulk chemical analysis, surface area analysis and cation exchange capacity will be known to those skilled in the art.

*Example 2: Recycle of mixed caustic liquor from initial reaction.*

120kg of the liquor containing both KOH and KCl from the reaction in Example 1 is retained for transfer back to the reaction tank. The reaction tank is topped up with 254kg

of caustic (comprising 59.1kg of KOH, 54.2kg of KCl and 141.4L of water) and pre-heated to 95°C. 75kg of kaolin (Kingwhite 65, supplied by Unimin Pty Ltd, Kingaroy, QLD Australia) is added to the caustic liquor, mixed thoroughly for 5.5 to 6.5 hours while maintaining the reaction temperature at 95°C  $\pm$  5°C. After 5.5 to 6.5 hours, the reaction tank is cooled to less than 50°C and the resulting slurry is separated into solid and liquid components using a filter press. The solid is washed with water and then dried using conventional drying methods (such as a spray dryer) to form the final product with properties listed in Tables 4 and 5.

The same procedure given above is repeated for the next seven reactions using the respective masses of caustic recycle and caustic make-up for each run as listed in Table 7. This example of the first recycle of caustic is defined as Run 2 in Table 7. The properties of the resultant zeolite N from each batch reaction using recycled liquor are listed in Tables 4 and 5. Figure 2 shows cation exchange capacities determined for each zeolite N produced by the recycling of caustic liquor and the evolution of CEC values as the reaction proceeds to completion (Examples 1 and 2).

*Example 3: Variation of process for zeolite N production – time and method of reaction.*

75kg of 98% solid potassium hydroxide (Redox Chemicals, caustic potash Capota45, QLD Australia), 75kg of 98% solid potassium chloride (Redox Chemicals, POCHLO16, QLD Australia), 250 litres of water supplied by a conventional domestic reticulated system and 75kg of kaolin (Kingwhite 65, supplied by Unimin Pty Ltd, Kingaroy, QLD Australia) are placed in a 500L stainless steel reactor tank. This reaction mix or viscous slurry is stirred and heated to 95°C over a period of seven hours. Once the slurry is at 95°C, the reaction is maintained at 95°C  $\pm$  3°C for a further nine hours and then cooled to less than 50°C to stop the reaction. The resulting slurry is separated using a filter press into solid and liquid components. The solid aluminosilicate – zeolite N – is washed with water and then dried using conventional drying methods (such as a spray dryer) to form the final product with properties listed in Tables 4 and 5.

*Example 4: Variation of process for zeolite N production – excess KOH with other chloride salt.*

75kg of 98% solid potassium hydroxide (Redox Chemicals, caustic potash Capota45, QLD Australia), 30kg of 98% solid sodium chloride (Cheetham Salt, Superfine grade, Australia), and 180 litres of water supplied by a conventional domestic reticulated system are placed in a 500L stainless steel reactor tank. This caustic solution is stirred and heated to 95°C. While the solution is at this temperature, 60kg of kaolin (Kingwhite 65, supplied by Unimin Pty Ltd, Kingaroy, QLD Australia) is added to the reaction mix while

stirring the solution. The reaction mix experiences a slight drop in temperature (to  $\sim 90^{\circ}\text{C}$ ) during the loading of kaolin. Depending on the quality of heating process employed, the reaction mixture may show temperature fluctuations of up to  $5^{\circ}\text{C}$  without significant loss of product quality. Small quantities of solid materials (approximately 50g) from the reaction mix are sampled at hourly intervals during this reaction and are characterised by conventional methods.

The reaction tank is partially covered with a stainless steel lid to aid with retention of heat and vapour(s). The reaction tank is maintained at ambient pressure during the production process. The pH of this reaction mix is generally greater than 13.0 and during the course of the reaction reduces by approximately 0.1 unit. During the reaction process – approximately 1.5 hours to 3.5 hours after the kaolin has been added to the reactor – the viscosity of the mixture increases. Addition of small amounts of water at this time to aid mixing of the slurry may be undertaken though it is not necessary to achieve production of zeolite N.

After 6.0 hours of reactant mixing at temperatures  $95^{\circ}\text{C} \pm 5^{\circ}\text{C}$ , the reaction is stopped by reduction of the temperature to less than  $50^{\circ}\text{C}$  (via cooling coils), addition of water or both methods and the resulting slurry is separated using a filter press into solid and liquid components. The solid aluminosilicate – zeolite N – is washed with water and then dried using conventional drying methods (such as a spray dryer) to form the final product with properties listed in Tables 4 and 5. Characterisation of the material using standard methods such as X-ray diffraction, bulk chemical analysis, surface area analysis and cation exchange capacity will be known to those skilled in the art.

*Example 5: Variation on zeolite N process – excess KOH with two chloride salts.*

660g of 98% solid potassium hydroxide (Redox Chemicals, caustic potash Capota45, QLD Australia), 660g of solid potassium chloride (Redox Chemicals, POCHLO16, QLD Australia), 259g of 98% solid sodium chloride (Cheetham Salt, Superfine grade, Australia), and 2.21 litres of water supplied by a conventional domestic reticulated system are placed in a 5L stainless steel reactor tank. This caustic solution is stirred and heated to  $95^{\circ}\text{C}$ . While the solution is at this temperature, 660g of kaolin (Kingwhite 65, supplied by Unimin Pty Ltd, Kingaroy, QLD Australia) are added to the reaction mix while stirring the solution.

The reaction is undertaken substantially as described in Example 1 for a period of 6.0 hours at  $95^{\circ}\text{C}$ . The solid aluminosilicate – zeolite N – is washed with water and then dried using conventional drying methods (such as a spray dryer) to form the final product with properties listed in Tables 4 and 5.

Example 6: Variation on zeolite N process – excess potassium and two chloride salts.

165g of 98% solid potassium hydroxide (Redox Chemicals, caustic potash Capota45, QLD Australia; that is, less than the stoichiometric amount), 165g of solid potassium chloride (Redox Chemicals, POCHLO16, QLD Australia), 235g of solid sodium hydroxide (Redox Chemicals, QLD Australia), 259g of 98% solid sodium chloride (Cheetham Salt, Superfine grade, Australia), and 2.21 litres of water supplied by a conventional domestic reticulated system are placed in a 5L stainless steel reactor tank. This caustic solution is stirred and heated to 95°C. While the solution is at this temperature, 660g of kaolin (Kingwhite 65, supplied by Unimin Pty Ltd, Kingaroy, QLD Australia) are added to the reaction mix while stirring the solution.

The reaction is undertaken substantially as described in Example 1 for a period of 6.0 hours at 95°C. The solid aluminosilicate – zeolite N – is washed with water and then dried using conventional drying methods (such as a spray dryer) to form the final product with properties listed in Tables 4 and 5.

X-ray diffraction peaks for this sample collected after six hours reaction show that the zeolite N phase is less crystalline than other preparation methods. Monitoring the progress of this reaction suggests that the reaction has first formed sodalite and other unidentified phases and that complete transformation to >90% zeolite N requires additional reaction time at the chosen temperature. Inspection of this product via SEM shows that zeolite N is the primary phase present and that minor amounts of sodalite is also present. Table 4 shows that the CEC value for this incompletely reacted product is less than values for products in Examples 1 to 5.

Example 7: Limit of zeolite N production with small excess of potassium.

660g of 98% solid potassium hydroxide (Redox Chemicals, caustic potash Capota45, QLD Australia), 518g of 98% solid sodium chloride (Cheetham Salt, Superfine grade, Australia), and 2.21 litres of water supplied by a conventional domestic reticulated system are placed in a 5L stainless steel reactor tank. This caustic solution is stirred and heated to 95°C. While the solution is at this temperature, 660g of kaolin (Kingwhite 65, supplied by Unimin Pty Ltd, Kingaroy, QLD Australia) are added to the reaction mix while stirring the solution.

The same procedure to achieve a dried powder as described in Example 6 is used for the product obtained after eight hours of reaction. Characterisation of the material using standard methods such as X-ray diffraction, bulk chemical analysis, surface area analysis and cation exchange capacity will be known to those skilled in the art.

X-ray diffraction peaks for this sample after eight hours reaction show that the zeolite N phase does not form. The X-ray data show that the crystalline phase formed is primarily sodalite with minor amounts of amorphous alumino-silicate material. Inspection of this reaction product via SEM shows that sodalite is the primary phase present and that a fine-grained material is also present.

**Example 8:** Variation on zeolite N process –  $55 < H_2O/Al_2O_3 < 65$

600g of 98% solid potassium hydroxide (Redox Chemicals, caustic potash Capota45, QLD Australia), 650g of 98% solid potassium chloride (Redox Chemicals, POCHLO16, QLD Australia), 2.1 litres of water supplied by a conventional domestic reticulated system and 500g of kaolin (Kingwhite 65, supplied by Unimin Pty Ltd, Kingaroy, QLD Australia) are placed in a 5L stainless steel reactor tank. This reaction mix or viscous slurry is stirred and heated to 95°C over a period of fourteen hours. Once the slurry is at 95°C, the reaction is maintained at 95°C  $\pm$  3°C for a further nine hours and then cooled to less than 50°C to stop the reaction. The resulting slurry is separated using a filter into solid and liquid components. The solid aluminosilicate – zeolite N – is washed with water and then dried using conventional drying methods (such as a spray dryer) to form the final product with properties listed in Tables 4 and 5.

**Example 9:** Exchange of potassium zeolite N to sodium zeolite N form.

20kg of zeolite N formed by the process described in Example 4 are placed in a stainless steel reaction tank and thoroughly mixed with 2M NaOH solution for two hours at room temperature (~25°C). The solid and liquid are separated via conventional means (e.g. a filter press or by sedimentation/decanting). The solid is washed thoroughly in water and then dried by conventional means (e.g. spray dryer). The solid shows partial exchange of potassium ions for sodium ions and the properties listed in Tables 4 and 5. Further exchange of potassium and sodium ions in zeolite N is effected by additional exchanges of the form described in this example. Complete exchange of sodium for potassium ions in the structure may require three or more exchanges with NaOH solution or longer times for the exchange process.

**Example 10:** Exchange of potassium zeolite N to ammonium zeolite N form.



20kg of zeolite N formed by the process described in Example 3 are placed in a stainless steel reaction tank and thoroughly mixed with 5M  $\text{NH}_4\text{NO}_3$  solution held at temperatures between 65°C and 80°C for two hours. The solid and liquid are separated via conventional means (e.g. a filter press or by sedimentation/decanting), the solid is washed thoroughly in water and then subjected to a second and third exchange using 5M  $\text{NH}_4\text{NO}_3$  solution held at temperatures between 65°C and 80°C for two hours. The solid is washed thoroughly in water and dried by conventional means (e.g. spray dryer). The solid shows exchange of potassium ions for ammonium ions and the properties listed in Tables 4 and 5, Example 10. X-ray diffraction shows the primary phase present is of a zeolite N structure although minor amounts (<5%) of kaliophillite are present. Almost complete exchange of potassium ion is demonstrated by the bulk analysis ( $\text{K}_2\text{O}=0.46$  wt%) and high value for loss-on-ignition determination ( $\text{LOI}=23.08\text{wt}\%$ ).

*Example 11: Use of Zeolite N for ammonium ion removal from an aqueous solution in the presence of calcium and magnesium at typical levels for municipal and industrial wastewaters.*

Zeolite 4A (PQ Corporation) and clinoptilolite (Australian Zeolites) were chosen as comparative zeolites for these examples. Zeolite 4A is the most widely produced synthetic zeolite and has a theoretically high cation exchange capacity due to a low Si:Al ratio. Clinoptilolite, the most commonly used natural zeolite, is recognized, as noted in prior art, to be of potential application in the area of ammonium ion exchange. Basic data for zeolite 4A are given in Table 8.

Approximately 0.2 g of zeolite material was equilibrated at room temperature for 1 hour with 200mL of an aqueous solution comprising ammonium, calcium and magnesium ions at the concentrations indicated in Table 9.

The results from treating the solutions listed in Table 9 with the various zeolites are tabulated in Table 10 and shown graphically in Figure 3.

The data in Table 10 reveal that zeolite N is characterized by a high loading capacity for ammonium ions in the presence of calcium and magnesium ions. In contrast, zeolite A, with a theoretical high value for ammonium ions, was found to be non-selective towards ammonium ions in the presence of calcium and magnesium ions. Furthermore, the data for clinoptilolite shows that calcium and magnesium ion concentration actually increases when this material is added to the test solution. Notably, for clinoptilolite the CEC value for ammonium ions is considerably lower than the value recorded for zeolite N.

A detailed evaluation of the selectivity characteristics for zeolite N in the sodium exchanged form (zeolite Na-N) and zeolite 4A was made by examining the quantity of

ammonium loaded on each zeolite sample as a function of ammonium ion in solution. The percentage selectivity as demonstrated in Figure 4 is defined as

$$\% \text{ selectivity} = (\text{CEC}_{\text{NH}_4^+} / \text{CEC}_{\text{tot of zeolite}}) \times 100 \quad (4)$$

where total  $\text{CEC}_{\text{tot}} = \text{CEC for calcium} + \text{CEC for magnesium} + \text{CEC for ammonium}$  and  $\text{CEC}_{\text{NH}_4^+} = \text{CEC for ammonium ion}$ .

The values plotted in Figure 4 clearly show the higher selectivity of zeolite Na-N for ammonium over alkali metal ions compared to zeolite 4A. This selectivity is a critical property for commercial application for ammonia removal in typical wastewater streams.

*Example 12: Use of zeolite N for ammonium ion removal from an aqueous solution in the presence of high calcium and magnesium.*

Example 11 demonstrated the higher selectivity of zeolite N for removal of ammonium ions from a solution comprising 50 mg/L calcium ions and 20 mg/L magnesium ions. In some wastewaters, the calcium ion concentration may be significantly higher than 50 mg/L. To demonstrate that zeolite N can be selective towards ammonium ion exchange in the presence of higher calcium ion concentrations, procedures similar to those described in Example 11 were performed with the solution compositions listed in Table 11.

Examination of the data in Table 12 reveals that zeolite N shows a high loading capacity for ammonium ions in the presence of 120 mg/L calcium ions. These data are presented graphically in Figure 3. For solutions containing 1,000 mg/L ammonium ions, the loading values for ammonium ion are 444 meq/100g and 451 meq/100g for zeolite K-N and zeolite Na-N, respectively, when 50 mg/L calcium ions are present and 475 meq/100g and 434 meq/100g for zeolite K-N and zeolite Na-N, respectively, when 120 mg/L calcium ions are present. Consequently, zeolite N is an excellent material for ammonium ion exchange capacity and ammonium ion selectivity.

In contrast, the performance of zeolite 4A is detrimentally affected by the presence of additional calcium ions in solution. For solutions containing 1,000 mg/L ammonium ions, the loading value for zeolite 4A is 261 meq/100g when 50 mg/L calcium ions are present and 192 meq/100g when 120 mg/L calcium ions are present. This represents a drop of over 25% in the performance of zeolite 4A in the presence of competing Ca and Mg ions. Therefore, zeolite 4A is unsuited to ammonium ion exchange in typical wastewater compositions with Ca and Mg present.

Clinoptilolite did not show any appreciable exchange for ammonium in the presence of calcium and magnesium ions with an increased concentration of calcium ions to 120 mg/L. However, the loading value for ammonium ions is low under all conditions (over 4 times lower than for zeolite K-N). Clinoptilolite does not offer properties suited to commercial treatment of wastewaters for removal of ammonium ions in the presence of  $\text{Ca}^{+2}$  and  $\text{Mg}^{+2}$ .

Further evaluation of the selectivity characteristics for zeolite Na-N, zeolite Na-F and for zeolite Na-A can be achieved by comparison of the ammonium loaded onto each zeolite sample as a function of ammonium ion in solution. For this comparison, percentage selectivity is defined as per equation (4) above. These values of selectivity are shown in Figure 4. Figure 4 clearly shows the higher selectivity of zeolite Na-N for ammonium in the presence of alkali metal ions compared to zeolite 4A. This higher selectivity by zeolite Na-N is a factor of at least two times that of zeolite 4A under the same conditions and is higher than zeolite Na-F at both concentrations of competing  $\text{Ca}^{2+}$  ion (i.e. 50mg/L and 120mg/L). This higher selectivity is a critical property for commercial application in wastewater streams.

While not wishing to be bound by theory, similar comparisons with other zeolites (e.g. zeolite Na-P and zeolite X) with regard to selectivity for ammonium ions will show that zeolite N has a higher performance.

***Example 13: Ammonium exchange capacity for zeolite N granules with regeneration.***

A bed of zeolite K-N granules (material prepared as in Example 1; 1mm-3mm average diameter granules) is placed in 50mm diameter glass columns with packed height approximately 750mm. A synthetic solution containing 994mg/L  $\text{NH}_4^+$  is introduced to the columns via variable speed pumps at flow rates ranging from 1.2 l/hr to 10.5 l/hr. The solutions are pumped in a down-flow direction for ammonia loading and in an up-flow direction during regeneration. Determination of the optimum regenerant solution for ammonium-loaded zeolite N is provided in Example 14.

The concentration of ammonium ion in the outflow after pumping through the column and the volume of solution treated to achieve full ammonia loaded material is measured. A fully-loaded zeolite N is determined when the outflow ammonium ion concentration is less than 5% of the inflow ammonium ion. Solution flow-rates for the high ammonium ion concentration (994mg/L) are 3 bed volumes per hour which is equivalent to a hydraulic residence time of 20 minutes. Measurements of ammonium ion concentration in the regenerant solution allow calculation of an effective loading capacity for each loading cycle.

A similar procedure is undertaken for the natural zeolite, clinoptilolite, obtained from Australian Zeolites Pty Ltd to provide comparative data. The values for effective loading capacity for each material under these operating conditions in a fixed bed column are given in Table 13.

For lower concentrations of ammonium ion, a synthetic solution containing 30mg/L  $\text{NH}_4^+$  is also used to load ammonium onto the fixed bed zeolite N column. The solution flow-rates for low ammonium concentration are 29 bed volumes per hour which is equivalent to a hydraulic residence time of 2 minutes. Loading capacity data for two cycles are also shown in Table 13.

Effective loading capacity is a convenient comparative measure of engineering or commercial significance in that design factors (e.g. volume of material required for ammonia removal; size of columns for ion exchange) can be determined. The data in Table 13 show that zeolite N is a superior material for ammonium ion removal in a fixed bed exchange column and is at least 30x to 50x more effective than the natural zeolite, clinoptilolite.

***Example 14:** Ammonium exchange capacity for zeolite N granules for solutions containing  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .*

Fixed bed columns as described in Example 13 are used to measure effective loading capacity for zeolite N granules contacted with a solution containing 1,000mg/L  $\text{NH}_4^+$ , 120mg/L  $\text{Ca}^{2+}$ , 30mg/L  $\text{Mg}^{2+}$  and 240mg/L  $\text{CO}_3^{2-}$  ions. The columns are filled with zeolite N prepared by the method described in Example 3. Data for two granulated forms with approximately 15% binder using methods for extrusion known to those skilled in the art are shown in Table 14. In each case, the granules are loaded with ammonium to fully-loaded condition (i.e. when the outlet ammonium concentration is less than 5% that of the inlet concentration) and the loading capacity is determined. Table 14 shows that a high loading capacity is achieved for zeolite N even in the presence of calcium and magnesium ions. Comparison of loading capacities with those in Table 13 shows that the values are similar for inlet ammonium concentrations ~1,000mg/L and thus, verifies that zeolite N is selective for ammonium ion in the presence of calcium and magnesium ions.

***Example 15:** Comparison of zeolite N capacity with other zeolites.*

Sherman and Ross (US 4,344,851) have compared the ammonium ion removal capacity for potassic zeolites tested in a fixed bed exchange column at low ammonium ion concentrations (15mg/L) over four regeneration cycles. A similar fixed bed evaluation has

been carried out for zeolite N under comparable, but not identical, conditions. The work by Sherman and Ross plots a comparison of ammonium capacity (in bed volumes) for regeneration cycles for zeolites K-W, K-F and clinoptilolite. Using data for an inlet ammonium ion concentration of 30mg/L at a flow-rate of 29bed volumes per hour, the performance of zeolite N over two regenerations is plotted in Figure 5 (modelled after Figure 1 of Sherman, 1975).

Comparison of data in Figure 5 shows that zeolite N has a higher capacity for ammonium ion in low concentration solutions (*i.e.* < 30mg/L) than either zeolite F or zeolite W. In addition, similar to the case for zeolite W, the capacity increases on the second cycle of regeneration. However, zeolite N capacity remains more than three times higher than zeolite W or zeolite F after the first regeneration. Corrections for differences in flow-rates and ammonium ion concentration are presented in Figure 5 as data points joined by dotted lines. These points show that the estimated capacity for zeolite N under the same conditions as zeolites W and F is significantly higher. This comparison, in accordance with the data shown in Figure 4 of Example 12, suggests that the capability of zeolite N to remove ammonium ion from solutions with low levels of ammonium is superior to that of zeolites W or F.

**Example 16:** *Regenerant composition for use with ammonium-loaded zeolite N (zeolite  $\text{NH}_4\text{-N}$ ).*

Prior art (US 3,723,308, US 4,344,851, US 4,695,387 and US 6,080,314) teaches that zeolites can be regenerated by a number of methods (including use of an alkaline solution or heating) but that for ammonium-loaded zeolites the most common method is the use of a caustic regenerant solution. In US 3,723,308 and US 4,344,851, the regeneration process uses a salt solution (usually sodium, potassium or calcium chloride or mixtures thereof) with addition of caustic (*e.g.* NaOH) to increase pH to remove ammonium ion loaded onto the zeolite and replace with an alkali metal ion. However, the use of salt solutions may not be chemically efficient for all zeolite types and the resultant brine solution can be difficult to dispose or re-use in an environmentally responsible and cost-effective manner.

A series of caustic solutions have been compared for regeneration of an ammonium-loaded zeolite N. The regenerant solution compositions include industrial grade NaOH (only), NaOH and NaCl, NaOH and  $\text{Na}_2\text{CO}_3$  in a range of concentrations. Ammonium loading of zeolite N on each cycle is with 1M  $\text{NH}_4\text{Cl}$  solution.

For regeneration cycles, 20g of ammonium loaded zeolite N is contacted with 80ml of regenerant solution in a 250mL Nalgene bottle with constant shaking for two hours. The

solution is centrifuged at 3,000rpm for five minutes and the amount of ammonium and pH of the supernatant is measured. For second and subsequent regenerations, the same procedure is used on re-loaded ammonium zeolite N. The removal rate of ammonium ion for each regenerant solution is determined by measurement of ammonium in the regenerant solution and on the solid sample before regeneration. Figures 6a and 6b show the effective ammonium removal rate as a % of total ammonium on the material for different ratios of NaOH+NaCl and NaOH+Na<sub>2</sub>CO<sub>3</sub> solutions.

The data in Figures 6a and 6b show that for both combinations of solutions as a regenerant, removal of ammonium can be achieved at all ratios of NaCl or Na<sub>2</sub>CO<sub>3</sub> to NaOH. This outcome is consistent with teachings from prior art. However, a higher removal rate (*i.e.* > 75%) for ammonium ion occurs for ratios in which NaOH is present at more than 0.4M. Furthermore, these data show that the best removal rate occurs for NaOH only solutions and that ammonium-loaded zeolite N is suited to regeneration by NaOH only solutions held at high pH (*i.e.* greater than 12) without degradation of the material.

The use of NaOH only solutions for regeneration has significant commercial and environmental benefits in that (a) salt or brine solutions do not accumulate during repetitive regeneration steps, (b) the amount of caustic required to drive the exchange equilibrium is determined by the "top-up" requirement associated with exchange mass balance (*i.e.* replacement of NH<sub>4</sub><sup>+</sup> for Na<sup>+</sup> in the zeolite N structure) and (c) re-use of the caustic for additional regeneration steps is readily achieved.

The range of NaOH concentrations for which an effective removal rate can be achieved from ammonium-loaded zeolite N is shown in Figure 7. At low molarity (0.1M), the removal rate is low at 40%. However, at higher molarity and, specifically above 0.4M NaOH, the removal rate is greater than 85% for the first regeneration and higher for the second regeneration. In this instance, the form of zeolite N is potassic for the first cycle of loading/regeneration and sodic for the second cycle of loading/regeneration. For subsequent regenerations, removal rates of >90% are maintained when the molarity is > 0.4M.

This comparison of regeneration solutions shows that ammonium-loaded zeolite N is ideally suited to regeneration by sodium-rich solutions and, in particular, by NaOH solutions with molarity greater than 0.4. This result is in contrast to that of Breck (US 3,723,308) who showed that a saturated lime solution with sodium chloride and calcium chloride is a suitable regeneration solution for zeolite F and Sherman and Ross (US 4,344,851) who used 1.0N NaCl with NaOH (adjusted to pH 12.0) to regenerate zeolites W and F. The data in Figure 7a show that for NaCl/NaOH solutions with pH ~ 12.0 at

high NaCl molarity, the ammonium removal rate is significantly less than a NaOH only solution (i.e. 32% vs 84% on first cycle; 62% vs 94% on second cycle).

*Example 17: Use of Zeolite N for ammonium ion removal from an aqueous solution in the presence of calcium, potassium and sodium ions at typical levels for ruminal fluid.*

Zeolite 4A (PQ Corporation) and clinoptilolite (Australian Zeolites) were chosen as comparative zeolites for these examples. Zeolite 4A is the most widely produced synthetic zeolite and has a theoretically high cation exchange capacity due to a low Si:Al ratio. Clinoptilolite, the most commonly used natural zeolite, is recognized, as noted in prior art, to be of potential application in the area of ammonium ion exchange.

Approximately 0.2 g of zeolite material was equilibrated at room temperature for 1 hour with 200 mL of an aqueous solution comprising 1000mg/L ammonium, 100mg/L calcium, 2,000mg/L potassium and 2,000mg/L sodium ions.

The results from treating this latter solution with the various zeolites are tabulated in Table 15.

The data in Table 15 reveals that zeolite N is characterized by a high loading capacity for ammonium ions in the presence of calcium, sodium and potassium ions (a positive value for loading shows that ions are adsorbed by the material of interest, whereas a negative value shows that ions are released into the solution by the material of interest). In contrast, zeolite 4A, with a theoretical high loading for ammonium ions, was found to be non-selective towards ammonium ions in the presence of calcium, sodium and potassium ions. Furthermore, the data for clinoptilolite is unusual in that calcium and magnesium ion concentration actually increases when this material is added to the tested aqueous solution. Notably, for clinoptilolite the value for ammonium ions is considerably lower than the value recorded for zeolite N.

The percentage selectivity as demonstrated in Table 14 is defined for ammonium, for example, as:

$$\% \text{ selectivity} = (\text{CEC}_{\text{NH}_4^+} / \text{CEC}_{\text{tot}} \text{ of zeolite}) \times 100$$

(5)

where total  $\text{CEC}_{\text{tot}} = \text{CEC for calcium} + \text{CEC for ammonium} + \text{CEC for sodium} +/\text{or CEC for potassium}$  and  $\text{CEC}_{\text{NH}_4^+} = \text{CEC for ammonium ion}$ . The choice of sodium or potassium ions in equation (5) depends upon which of these ions is adsorbed by the material of interest.

Table 15 also shows data for the excess ions in solution. This value is calculated from the measured concentrations of ions in solution after the material of interest has been

added. The low value for excess ions in all cases indicates that ion exchange (rather than precipitation of insoluble phases) occurs under these experimental conditions.

The values presented in Table 15 clearly show the higher selectivity of zeolite N for ammonium over alkali metal ions compared to zeolite 4A, zeolite F and clinoptilolite. This selectivity is a critical property for commercial application for ammonia concentration control in ruminant animals.

***Example 18:** Use of Zeolite N for copper, cadmium or nickel ion removal from an aqueous solution in the presence of calcium ions at typical levels for wastewater solutions.*

Zeolite 4A (PQ Corporation), Zeolite Na-F and clinoptilolite (Australian Zeolites) were chosen as comparative zeolites for these examples. Zeolite 4A is the most widely produced synthetic zeolite and has a theoretically high cation exchange capacity due to a low Si:Al ratio. Zeolite F is proposed to be more selective than Zeolite A in prior art and has an Si:Al ratio of ca. 1.

Approximately 0.2 g of zeolite material was equilibrated at room temperature for 1 hour with 200 mL of an aqueous solution comprising 50 mg/L of the appropriate metal ion (e.g. copper, cadmium or nickel) and 200 mg/L calcium ions.

The results from treating this latter solution with the various zeolites are tabulated in Table 16.

The data in Table 16 reveals that zeolite N is characterized by a high loading capacity for copper ions in the presence of calcium ions (a positive value for loading shows that ions are adsorbed by the material of interest, whereas a negative value shows that ions are released into the solution by the material of interest). Similarly, zeolite 4A and zeolite Na-F also show comparable values for loading capacity for copper ions. Clinoptilolite is found to be a very poor material for exchange of copper ions from aqueous solution.

However, the calcium ion uptakes are significantly different in value for these materials. Zeolite 4A exchanges large quantities of calcium ions, whereas zeolite Na-F exchanges significantly less calcium ions compared with zeolite 4A. However, the performance of zeolite N which exhibits the lowest exchange of calcium ions in the presence of copper ions shows that the material has high selectivity for small-sized metal ions.

Table 16 also compares the copper selectivity values for zeolite N relative to Zeolite 4A, Na-F and Clinoptilolite. The data in Table 16 show that zeolite N is highly selective



towards copper ion in the presence of excess amounts of competing calcium ions in solution.

Similar data are obtained for the cadmium/calcium and nickel/calcium system and are also shown in Table 16. The values for cadmium loading onto zeolite N are lower than for copper ion loading, but again, the selectivity of zeolite N for cadmium ions over calcium ions is high ( $> 80\%$ ) as shown in Table 16. These selectivity values for cadmium are higher than that for zeolite Na-F and significantly higher than the value for zeolite 4A. The selectivity value for clinoptilolite – whilst 100% – has little practical value as the loading capacity is extremely poor ( $< 1\text{ meq}/100\text{g}$ ).

Table 16 lists data for nickel adsorption and shows that zeolite K-N is similar in loading capacity to zeolite Na-F but that zeolite Na-N shows a loading for nickel almost twice that of zeolite Na-F and significantly higher than zeolite 4A (by a factor of  $\sim 8$  times). The selectivity for nickel ions over calcium ions is also significantly higher for zeolite N than for zeolites F, 4A or clinoptilolite.

Table 16 also shows data for the excess ions in solution for each metal/alkali ion system. This value is calculated from the measured concentrations of ions in solution after the material of interest has been added. The low value for excess ions in all cases indicates that ion exchange (rather than precipitation of insoluble phases) occurs under these experimental conditions.

While not wishing to be bound by theory, similar selectivities for other metal ions such as zinc and cobalt can be attributed to zeolite N. These data confirm that zeolite N has strong potential for commercial application in water treatment for the removal of transition and heavy metal ions in the presence of alkali metal ions.

**Example 19:** *Capacity of zeolite N to absorb oil.*

5g of material (e.g. zeolite Na-N from Example 9) is kneaded by hand on a glass plate using a spatula with boiled linseed oil. The linseed oil is added dropwise from a burette and the amount required to achieve the end point is measured. The end point is determined as the point at which the 5g of material is completely saturated with oil and has a consistency of putty. The volume of oil required to achieve the end point is converted to weight of oil per weight of material (i.e.  $\text{g}/100\text{g}$ ). The results of these standard oil absorption tests on zeolite N samples from Examples 1, 4, 9 and 10 as well as commercially available materials are shown in Figure 8. Other materials tested are: (a) Alumina Hydrate (AS303 supplied by Commercial Minerals Ltd.), (b) Activebond 23 Bentonite (supplied by Commercial Minerals Ltd); (c) Zeolite 4A (supplied by PQ

Corporation), (d) Trubond MW Bentonite (supplied by Commercial Minerals Ltd.), (e) Kingaroy kaolin (Kingwhite 65, Unimin Aust., Pty Ltd), (f) attapulgite (Clay Minerals Society Source Clays: PF1-1 from Gadsen County FL) (g) zeolite K-N from example 1, (h) zeolite K,Na-N from example 4 and (i) zeolite Na-N from example 8. Figure 8 shows that zeolite N in its various forms has high oil absorption capacity and significantly higher values than bentonites and zeolite 4A. Oil absorption capacity for zeolite N is similar to, or better than, zeolite X (for which property this material is used in detergents) and attapulgite. Bentonites, zeolite X and attapulgite are used commercially for oil absorption.

## Schedule of Tables

Table 1

Comparison of reaction conditions for zeolite N produced by this work and by prior art

Parameter	Christensen & Fjellvig (1997)	This Work (Example 1)	This Work (Example 4)	This Work (Example 5)	This Work (Example 6)	This Work (Example 8)
Batch Composition						
Material Type	Na-A	kaolin	kaolin	kaolin	kaolin	kaolin
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	2	2	2	2	2	2
K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	0	2.3	2.8	2.3	0.6	2.8
Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	1	0	0	0	2.9	0
H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	208	50	46	50	52	63
KCl/Al <sub>2</sub> O <sub>3</sub>	12.4	3.5	0	1.7	0.9	4.5
NaCl/Al <sub>2</sub> O <sub>3</sub>	0	0	2.2	1.7	1.7	0
Cl/SiO <sub>2</sub>	6.2	1.7	1.1	1.7	1.3	2.3
K/(K+Na) "Cation ratio"	0.8	1.0	0.7	0.8	0.2	1.0
(K+Na-Al)/Si "Excess alkalinity"	7.7	3.5	3.5	3.5	4.3	4.5
Temperature (°C)	300	95	95	95	95	95
Time (days)	7	0.25	0.25	0.25	0.25	0.6
Mass of Materials	135g	475kg	345kg	4.1kg	3.7kg	3.9kg
Batch Method(s)	Static; autoclave	Stirred; ambient P	Stirred; ambient P	Stirred; ambient P	Stirred; ambient P	Stirred; ambient P
Product	Zeolite N	Zeolite N	Zeolite N	Zeolite N	Zeolite N	Zeolite N

Table 2

Comparison of reaction conditions for selected zeolites produced by prior art

Parameter	Barrer et al. (1953)		Barrer and Marcilly (1970)		Barrer & Munday (1971)
Batch Composition					
Material Type	analclime	gel	Na-X	kaolin	kaolin
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	4	4	2.5	2	2
K <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	0	0.78	0	1	19.9
Na <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	1	0	1	0	0
H <sub>2</sub> O/Al <sub>2</sub> O <sub>3</sub>	88	>68	284	103	378
KCl/Al <sub>2</sub> O <sub>3</sub>	12	unknown	67	24.4	0
NaCl/Al <sub>2</sub> O <sub>3</sub>	0	0	0	0	0
Temperature (°C)	450	450	260	>200	80
Time (days)	2	1	4	4	12
Mass of Materials	< 15g	< 10g	<15g	<10g	27g
Batch Method(s)	Static; autoclave	Static; autoclave	Static; autoclave	Static; autoclave	Static; autoclave
Product	Leucite + Zeolite N	Kalsilite + Zeolite N	Zeolite F	kaliophilite	Zeolite F

**Table 3**  
Crystal Structure and Compositional Data for selected zeolites

Zeolite Type	Space Group	Framework Topology	Cell Dimensions	Composition	Si:Al Ratio	Reference
Zeolite K-N	I222	EDI Type	a=990.4; b=988.6; c=1309.0	$K_{12}(Si_{10}Al_{10}O_{40}) \cdot 8H_2O$	1.0	Christensen and Fjellvag, 1997
Zeolite K-F	P-421m	EDI Type	a=1038; c=1390	$K_5(Si_5Al_5O_{20}) \cdot 9H_2O$	1.0	US2,996,358
Zeolite Na-F	P-421m	EDI Type	a=1005.6; c=688.0	$Na_5(Si_5Al_5O_{20}) \cdot 9H_2O$	1.0	Baerlocher and Barrer, 1974
Zeolite Na-A	Fm-3c	LTA Type	a=2461.0	$Na_{96}(Si_{96}Al_{96}O_{384}) \cdot 216H_2O$	1.0	Gramlich and Meier, 1971
Zeolite Na-P	I-4	GIS Type	a=1004.3	$Na_8(Si_{10}Al_6O_{32}) \cdot 11H_2O$	1.7	Baerlocher and Meier, 1972
Zeolite K-W	Immm	MER Type	a=1409.5; b=1420.3; c=1004.2	$K_{10}(Si_{22}Al_{10}O_{84}) \cdot 20H_2O$	2.2	Bienlok <i>et al.</i> , 1996

**Table 4**  
Properties of zeolite N produced by examples

Sample No.	Refined Cell Dimensions (pm) (I222 Space Group)			No. of Peaks to fit	CEC <sup>+</sup> meq per 100g	S A m <sup>2</sup> /g	Particle Size d <sub>50</sub> : µm
	a	b	c				
Example 1	992.4(3)	989.3(4)	1311.4(3)	41	528	10.7	3.3
Example 2, Run 1	992.0(3)	985.6(3)	1309.2(3)	40	499	9.9	4.2
Example 2, Run 2	991.1(4)	987.5(3)	1308.5(4)	42	516	21.2	4.3
Example 2, Run 3	991.1(3)	987.2(3)	1309.4(4)	38	530	5.3	3.9
Example 2, Run 4	992.2(3)	988.5(4)	1310.8(5)	43	504	11.0	4.0
Example 2, Run 5	992.3(3)	988.9(4)	1311.2(3)	40	532	11.4	4.4
Example 2, Run 6	992.6(4)	987.7(4)	1310.7(5)	39	518	10.5	4.4
Example 2, Run 7	992.4(4)	989.2(4)	1310.6(4)	38	483	11.5	4.2
Example 2, Run 8	992.3(4)	988.6(5)	1310.5(5)	40	503	10.5	4.5
Example 3	992.3(3)	989.6(6)	1310.3(3)	38	518	14.8	2.5
Example 4	992.2(5)	988.3(5)	1308.8(7)	28	504	13.6	4.2
Example 5	992.3(4)	988.6(3)	1308.9(3)	38	503	12.4	7.4
Example 6	993.1(4)	988.9(4)	1308.6(5)	30	414	16.7	7.8
Example 8	na	na	na	na	506	7.4	
Example 9	992.9(3)	988.2(3)	1308.8(3)	38	510	15.5	2.32
Example 10	995.1(4)	989.4(6)	1315.3(9)	31	503	20.8	7.13

<sup>+</sup>CEC values determined for 1M NH<sub>4</sub>Cl equilibrium exchange as described under "Standard Procedures".

"na" = not available

**Table 5**  
Properties of zeolite N produced by examples

Sample No.	Reaction Mixture (Ratios to Al <sub>2</sub> O <sub>3</sub> )					m*	f*	Bulk Analyses of Zeolite N Product (weight %)				
	K <sub>2</sub> O	KCl	H <sub>2</sub> O	Na <sub>2</sub> O	NaCl			SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	LOI
Example 1	2.30	3.46	50.31	0.00	0.00	3.53	1.00	34.51	28.40	27.23	<0.5	7.24
Example 2, Run 1	2.30	3.46	50.31	0.00	0.00	3.53	1.00	33.40	26.60	23.15	<0.5	11.07
Example 2, Run 2	2.30	3.46	50.31	0.00	0.00	3.53	1.00	34.50	27.80	24.18	<0.5	7.59
Example 2, Run 3	2.30	3.46	50.31	0.00	0.00	3.53	1.00	34.60	28.00	24.42	<0.5	7.18
Example 2, Run 4	2.30	3.46	50.31	0.00	0.00	3.53	1.00	33.20	26.80	23.56	<0.5	10.74
Example 2, Run 5	2.30	3.46	50.31	0.00	0.00	3.53	1.00	33.40	27.00	23.39	<0.5	10.41
Example 2, Run 6	2.30	3.46	50.31	0.00	0.00	3.53	1.00	33.40	26.90	23.54	<0.5	10.69
Example 2, Run 7	2.30	3.46	50.31	0.00	0.00	3.53	1.00	34.40	27.80	24.67	<0.5	7.33
Example 2, Run 8	2.30	3.46	50.31	0.00	0.00	3.53	1.00	34.40	28.10	24.22	<0.5	7.63
Example 3	2.30	3.46	50.31	0.00	0.00	3.53	1.00	36.00	27.70	26.72	<0.5	6.89
Example 4	2.87	0.00	45.88	0.00	2.21	3.48	0.72	36.00	28.60	24.59	1.44	7.26
Example 5	2.30	1.73	50.31	0.00	1.73	3.53	0.78	na	na	na	na	na
Example 6	0.57	0.87	51.52	2.94	1.73	4.31	0.21	na	na	na	na	na
Example 8	2.78	4.50	62.97	0.00	0.00	4.51	1.00	na	na	na	na	na
Example 9	-	-	-	-	-	-	-	35.90	29.10	17.38	4.85	10.33
Example 10	-	-	-	-	-	-	-	41.02	32.67	0.46	<0.5	23.08

\*m = excess alkalinity calculated by the equation  $m = (K + Na - Al) / Si$

\*f = cation ratio calculated by the equation  $f = K / (K + Na)$

\*na = not available

**Table 6**  
Comparison of caustic use with and without recycling

Reactant Masses	Without Recycle	With Recycle
Mass of kaolin (kg)	675	675
Mass of caustic (kg)	1,350	821
Mass of zeolite N (kg)	783	783
Caustic:Product ratio	1.7	1.05

**Table 7**  
Data on caustic recycle for zeolite N production  
T ~ 95°C

Run No.	Caustic Recycle Source	Caustic Recycle Mass (kg)	Caustic Make-up Mass (kg)	Caustic Make-up %	CEC (meq/100g)
1	Example 1	0	0	0	515
2	Run 1	120	113	25	502
3	Run 2	260	97	23	488
4	Run 3	260	78	18	506
5	Run 4	250	77	18	510
6	Run 5	250	79	18	513
7	Run 6	230	75	18	518
8	Run 7	245	79	18	500
9	Run 8	250	73	17	501

**Table 8**  
Comparison of zeolite properties

Property	Zeolite 4A	Zeolite N (Example 3)
Si:Al	1	1
CEC* (meq/100g)	472	518
Surface area (m <sup>2</sup> /g)	2.26	14.8
Particle Size (μm)	4.3	2.5

\*CEC values determined for 1M NH<sub>4</sub>Cl equilibrium exchange as described under "Standard Procedures".

**Table 9**  
Solution compositions for Example 10

	Ammonium ion concentration (mg/L)	Calcium ion concentration (mg/L)	Magnesium ion concentration (mg/L)
Solution 1	30	50	20
Solution 2	200	50	20
Solution 3	1000	50	20

**Table 10**

Loading data for calcium, magnesium and ammonium ions on zeolites described in Example 10

	Solution 1	Solution 2	Solution 3
<b>Ca<sup>2+</sup> Loading (meq/100 g)</b>			
Zeolite 4A	229	236	206
Zeolite K-N	10	25	18
Zeolite Na-N	23	20	9
Clinoptilolite	17	4	15
<b>Mg<sup>2+</sup> Loading (meq/100 g)</b>			
Zeolite 4A	37	22	7
Zeolite K-N	4	0	0
Zeolite Na-N	5	0	0
Clinoptilolite	2	0	4
<b>NH<sub>4</sub><sup>+</sup> Loading (meq/100 g)</b>			
Zeolite 4A	68	172	261
Zeolite K-N	104	347	444
Zeolite Na-N	118	406	451
Clinoptilolite	8	76	71

**Table 11**  
Solution compositions for Example 11

	Ammonium ion concentration (mg/L)	Calcium ion concentration (mg/L)	Magnesium ion concentration (mg/L)
Solution 4	30	120	20
Solution 5	200	120	20
Solution 6	1000	120	20

**Table 12**  
Loading data for calcium, magnesium and ammonium ions on zeolites described in Example 11

	Solution 4	Solution 5	Solution 6
<b>Ca<sup>2+</sup> Loading (meq/100 g)</b>			
PQ Zeolite 4A	423	379	297
Zeolite K-N	16	32	28
Zeolite Na-N	25	29	16
Clinoptilolite	-9	-1	-6
<b>Mg<sup>2+</sup> Loading (meq/100 g)</b>			
PQ Zeolite 4A	10	4	-1
Zeolite K-N	3	1	0
Zeolite Na-N	5	0	0
Clinoptilolite	4	1	-6
<b>NH<sub>4</sub><sup>+</sup> Loading (meq/100 g)</b>			
PQ Zeolite 4A	34	112	182
Zeolite K-N	104	331	475
Zeolite Na-N	119	326	434
Clinoptilolite	8	54	115

**Table 13**  
Comparison of loading capacities for two different solutions at two different flow rates

	Loading Capacity (g/kg) [994mg/L NH <sub>4</sub> <sup>+</sup> ] Flow = 3BV/hr		Loading Capacity (g/kg) [30mg/L NH <sub>4</sub> <sup>+</sup> ] Flow = 29BV/hr	
	Zeolite N	Clinoptilolite	Zeolite N	Clinoptilolite
Loading Cycle 1	75.2	6.8	64.8	2.3
Loading Cycle 2	69.0	7.0	48.5	0.9

**Table 14**  
Loading Capacity for ammonium in the presence of Ca and Mg

	Loading Capacity (g/kg) [1,000mg/L NH <sub>4</sub> <sup>+</sup> with Ca <sup>2+</sup> and Mg <sup>2+</sup> ]	
	Zeolite N	Zeolite N
Loading Cycle 1	82.2	82.1
Loading Cycle 2	74.0	77.5
Loading Cycle 3	74.0	77.4
Loading Cycle 4	73.1	74.9
Loading Cycle 5	72.7	72.3

**Table 15**

Ammonium selectivity of zeolites in alkali-rich solution (Example 17)

	Zeolite K-N	Zeolite Na-N	Zeolite Na-F	Zeolite 4A	Clinoptilolite
NH <sub>4</sub> (meq/100g)	128	155	169	74	5
Ca (meq/100g)	5	10	40	24	-15
Na (meq/100g)	15	-117	-225	-209	9
K (meq/100g)	-160	-53	20	98	12
Excess Ions	-12	-5	4	-13	11
% Selectivity (NH <sub>4</sub> )	87	94	74	38	0

**Table 16**Metal ion selectivity of zeolites in presence of Ca<sup>2+</sup> (Example 18)

	Zeolite K-N	Zeolite Na-N	Zeolite Na-F	Zeolite 4A	Clinoptilolite
<b>Copper/Calcium</b>					
Loading Cu (meq/100g)	115	127	135	145	4
Loading Ca (meq/100g)	22	35	58	290	8
Total Adsorbed Ions	137	162	193	435	12
Total Released Ions	-133	-167	-242	-493	-9
Excess Ions	4	-5	-49	-58	3
% Selectivity (Cu)	84	79	70	33	32
<b>Cadmium/Calcium</b>					
Loading Cd (meq/100g)	45	63	69	81	1
Loading Ca (meq/100g)	10	13	46	385	0
Adsorbed Ions	55	76	115	466	1
Released Ions	-76	-104	-180	-498	-6
Excess Ions	-21	-28	-65	-30	-5
% Selectivity (Cd)	81	83	80	17	100
<b>Nickel/Calcium</b>					
Loading Ni (meq/100g)	35	62	39	8	4
Loading Ca (meq/100g)	28	35	76	456	0
Adsorbed Ions	63	97	115	464	4
Released Ions	-74	-113	-175	-487	-6
Excess Ions	-11	-16	-60	-23	-2
% Selectivity (Ni)	56	64	34	2	100



## Schedule of Figures

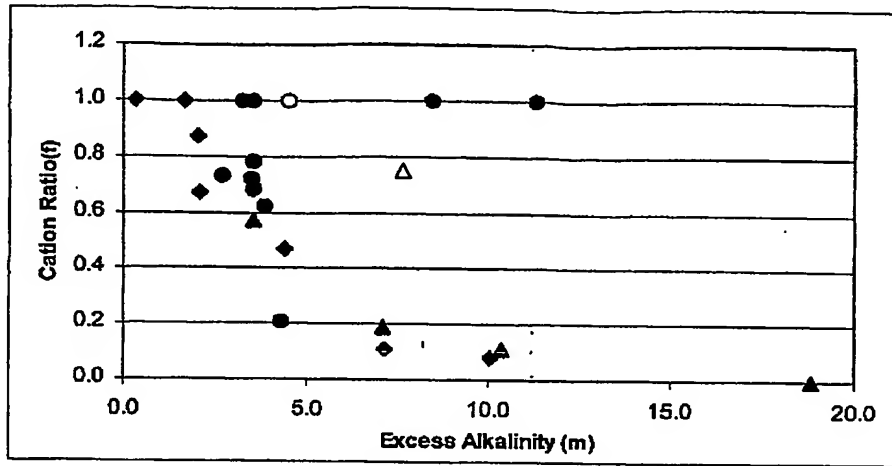


Figure 1a

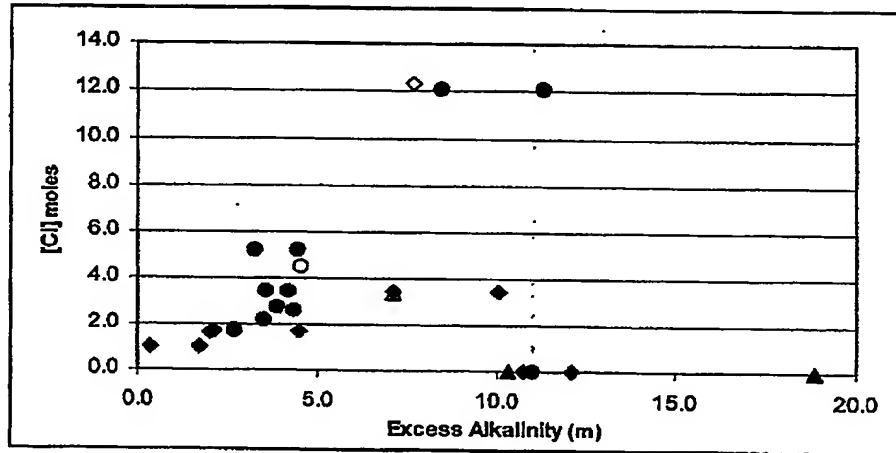


Figure 1b

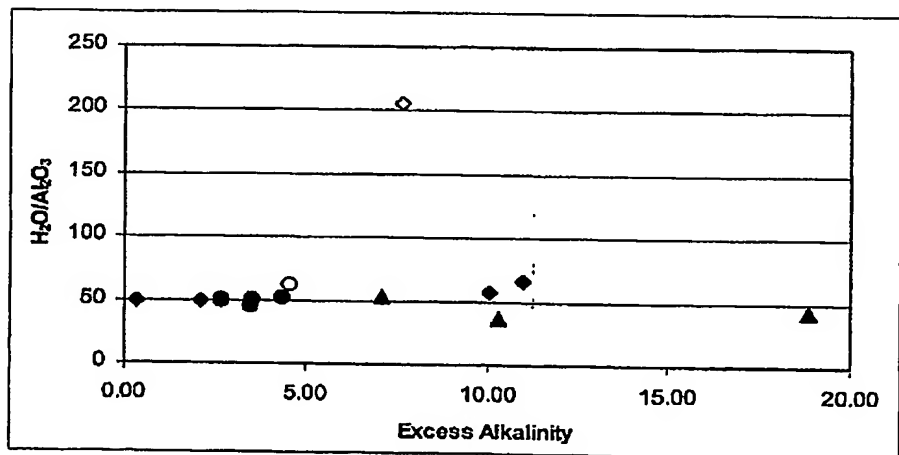


Figure 1c

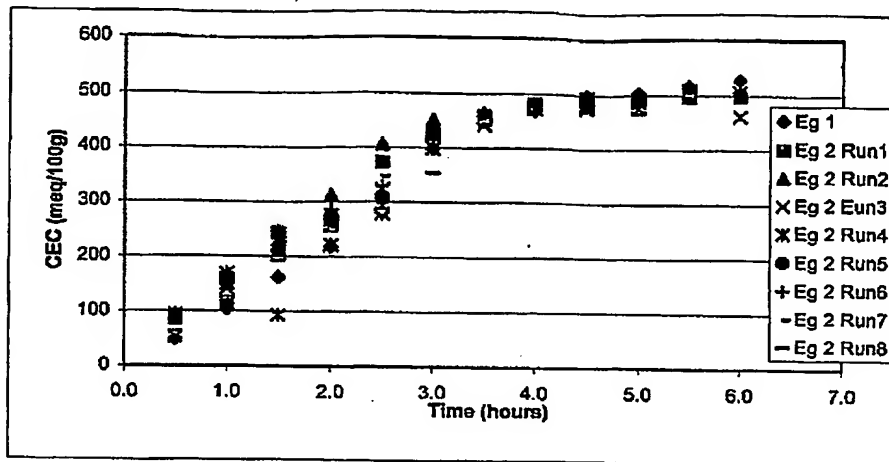


Figure 2

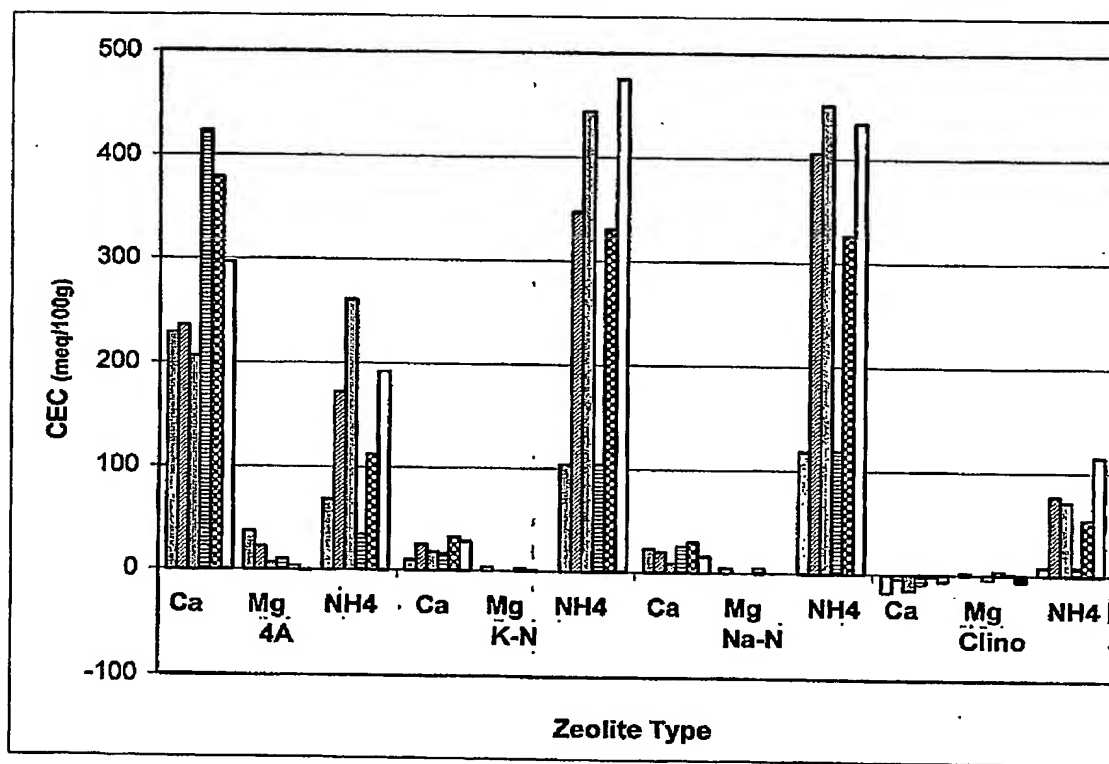


Figure 3

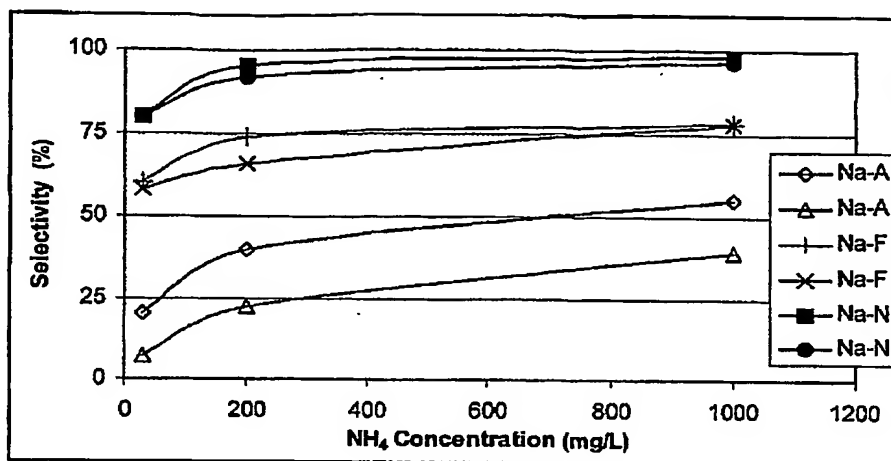


Figure 4

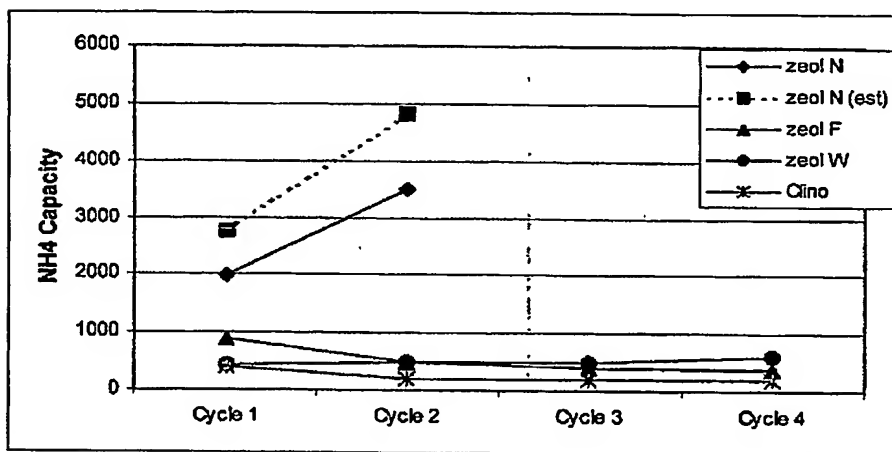


Figure 5

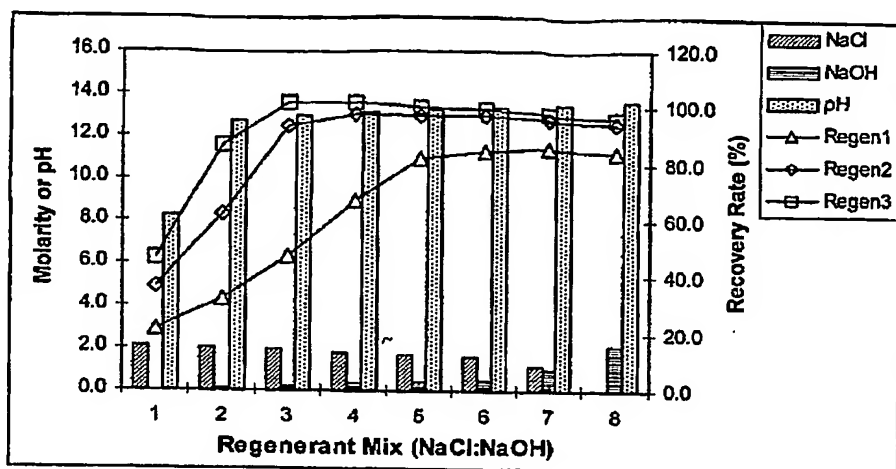


Figure 6a

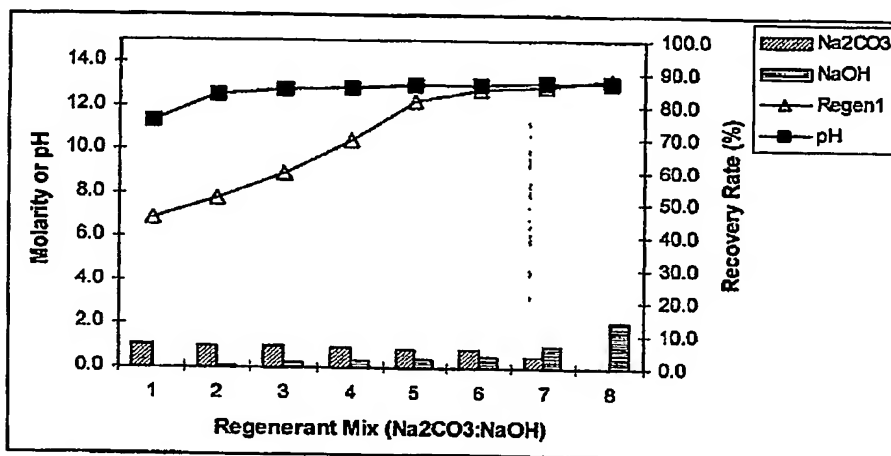


Figure 6b

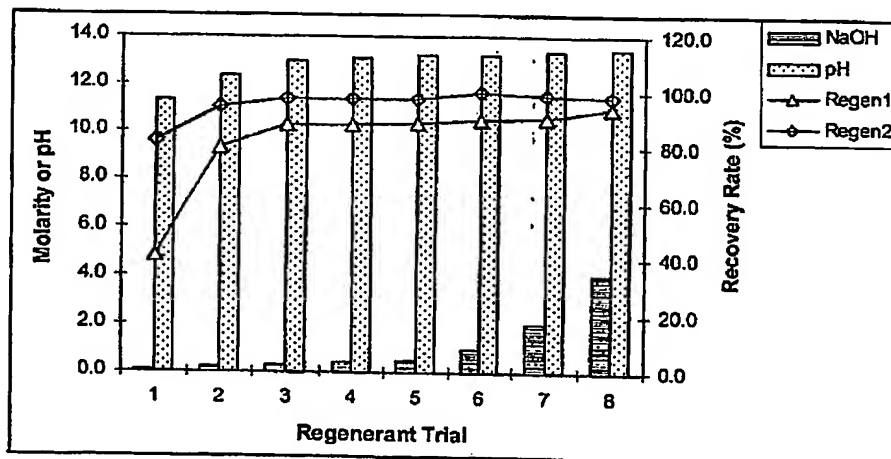


Figure 7

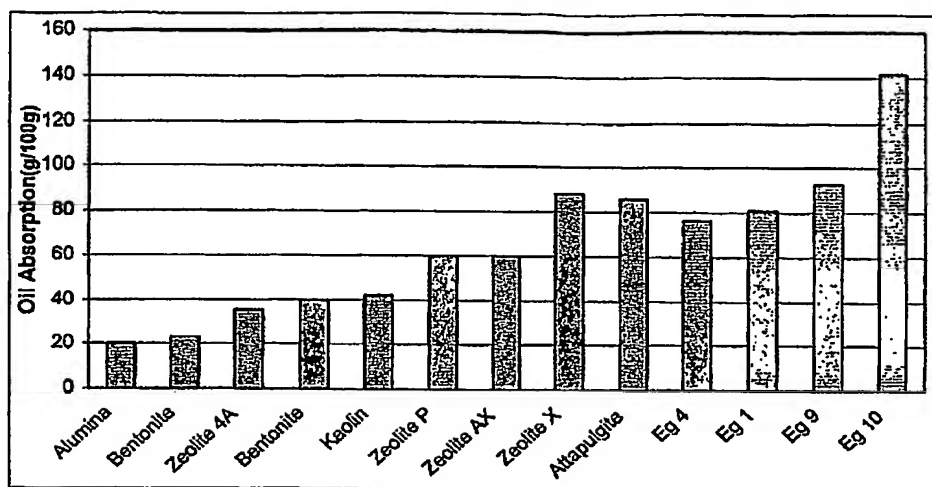


Figure 8

### Figure Captions

**Figure 1:** Compositions of the reactions used to produce zeolite N: (a) plot of cation ratio against excess alkalinity showing the region of zeolite N formation as described in Examples 1, 2, 4, 5 and 6 (filled circles); formation of other phases is shown by the filled diamond or filled triangle. Formation of zeolite N for  $55 < \text{H}_2\text{O}/\text{Al}_2\text{O}_3 < 65$  is shown with an open circle (Example 8). Reaction composition for the method by Christensen and Fjellvag (1997) is an open diamond. (b) formation of zeolite N for the same reactions in Figure 1(a) showing chloride ion concentration plotted against excess alkalinity. Symbols denote the same as in Figure 1(a). (c) formation of zeolite N for the same reactions in Figure 1(a) showing water content ( $\text{H}_2\text{O}/\text{Al}_2\text{O}_3$ ) plotted against excess alkalinity. Symbols denote the same as in Figure 1(a).

**Figure 2:** Dependence of CEC value with time of reaction for the method(s) described in Example 1 and Example 2. Zeolite N shows high CEC and is well formed between 4 hours and 6 hours reaction time using the conditions described for these examples.

**Figure 3:** CEC values for tests of ammonium selectivity in the presence of calcium and magnesium ions for zeolites 4A, K-N, Na-N and clinoptilolite as described in Examples 10 and 11. High ammonium ion CEC values for zeolites K-N and Na-N for all solution compositions are clearly shown. Solution compositions for each ion (Ca, Mg and  $\text{NH}_4$ ) follow that listed in Tables 9 and 11 (from left to right) Solutions 1 to 6.

**Figure 4:** Comparison of selectivity for ammonium ions for zeolites Na-A (denoted by open diamond and triangle), Na-F (denoted by "x" and "+") and Na-N (denoted by filled squares and circles) for 50mg/L and 120mg/L  $\text{Ca}^{+2}$  solutions as described in Example 11.

**Figure 5:** Comparison of ammonium absorption with regeneration cycles for zeolite N (filled diamond and square; this work), W, F and clinoptilolite (open circle, square and diamond; data from Sherman and Ross, 1982) as described in Example 14. The data points for zeolite N (est) are normalised to the experimental conditions used by Sherman and Ross (1982).

**Figure 6:** Comparative efficiency or recovery rate (%) for regenerant solutions when used with ammonium-loaded zeolite N as described in Example 15 for (a) NaCl-NaOH regenerant solutions and (b)  $\text{Na}_2\text{CO}_3$ -NaOH regenerant solutions.

**Figure 7:** Recovery rate (%) for regenerant NaOH solutions with different molarity when used with ammonium-loaded zeolite N. Two regeneration cycles are shown.

**Figure 8:** Comparison of oil absorption capacity (g/100g) for zeolite N from Examples 1, 4 and 8 and selected materials as described in Example 18.

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